

**BALL-MILLED PALM-DERIVED CARBON FOR
FABRICATION OF ELECTROCHEMICAL PHENOLIC
COMPOUND SENSORS AND SUPERCAPACITORS**

BY

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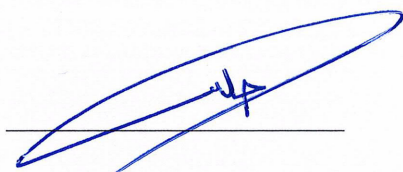
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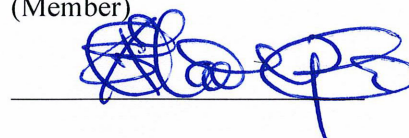
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Dedication

To

My beloved parents

My dear sisters and brothers

My faithful friends

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LIST OF ABBREVIATIONS

EESD	:	Electrochemical energy storage device
OPW	:	Operating potential window
BET	:	Brunauer–Emmett–Teller analysis
FESEM	:	Field emission scanning electron microscopy
XRD	:	X-ray diffraction analysis
EDS	:	Energy Dispersive Spectroscopy
FTIR	:	Fourier transform infrared
CV	:	Cyclic voltammetry
GCD	:	Galvanostatic charge discharge
EIS	:	Electrochemical impedance spectroscopy
GCE	:	Glassy carbon electrode

ABSTRACT

Full Name : Wael Mhd Amen Mahfoz

Thesis Title : Ball-milled palm-derived carbon for fabrication of electrochemical phenolic compound sensors and supercapacitors

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Abstract

A highly electroactive and low-cost electrode material is an essential requirement in the current sensor and supercapacitor research. To meet this demand, synthesizing biomass carbon through a simple process of pyrolysis and ball milling could be an ideal solution. In this work, active carbon was synthesized from the date leaves waste. The surface, structural, and compositional characterizations support the formation of sub-nano and nano-meter-size carbon particles. The synthesized carbon was successfully used for electrochemical phenolic compounds sensing and supercapacitor applications. The synthesized carbon was immobilized on a Glassy carbon electrode to fabricate a chemical sensor to detect 1-naphthol (1-NP) and 2-naphthol (2-NP) simultaneously. The study provides two methods to fabricate electrochemical sensors. The first method is based on the direct oxidation of 1-NP and 2-NP. The second method is based on redox peaks for the quinone formation from the generated dihydroxy naphthalene. The second method

shows a higher analytical performance toward simultaneous detection of 1-NP and 2-NP compared to that of the first method. In the second part of the thesis, a novel carbon was utilized by dispensing on a stainless-steel strip to fabricate a high-performance symmetric supercapacitor. The fabricated supercapacitor shows a double-layer capacitance behavior and a pseudocapacitance behavior due to the heteroatoms in the material. By using an electrolyte of (0.1 M sulfuric acid), the fabricated supercapacitor displays a high specific capacitance of (~ 107 F/g), and the stability test shows a capacitance retention of 92% after a total of 1000 cycles. Furthermore, the supercapacitor's densities of energy and power are ~ 10 Wh/Kg and ~ 200 W/Kg, respectively, offering an ideal supercapacitor for mass-product. This research provides a low-cost and high-performance supercapacitor based on cheap carbon prepared from the date leave waste. Furthermore, the work was supported with supplementary materials about the fabrication of supercapacitor prepared from stainless and electro-synthesized polyaniline (PANI). The fabricated supercapacitor combines the advantages of the low cost of the substrate and the high electrochemical performance of synthesized PANI. The supercapacitor shows an areal capacitance of ~ 353 mF cm⁻² and densities of energy and power of ~ 26.4 μ Wh cm⁻² and ~ 400 μ Wcm⁻² respectively. The capacitance properties were retained after 1000 cycles showing high stability. Based on the result, the fabricated supercapacitor could be an ideal candidate for wide applications and mass product in the future.

ملخص الرسالة

الاسم الكامل: وائل محمد امين محفوظ

عنوان الرسالة: الكربون المحضر من سعف النخيل بطريقة الطحن باستخدام الكرات لتحضير الحساسات الكهروكيميائية لمركبات الفنولات وللمكثفات الفائقة السعة

التخصص: الكيمياء

تاريخ الدرجة العلمية: مارس ٢٠٢٣

يعد الحصول على المادة المناسبة والمنخفضة التكلفة أحد أهم المتطلبات وأكثرها تحديًا في أبحاث المستشعرات الكهروكيميائية والمكثفات ذات السعة الفائقة. في هذا الصدد، يعتبر الكربون المحضر من الكتلة الحيوية عن طريق الانحلال الحراري والطحن باستخدام الكرات مادة مثالية للقطب الكهربائي للاستشعار التحليلي وتطبيقات المكثفات ذات السعة الفائقة. في هذا العمل، حُضر الكربون ذو أبعاد متناهية الصغر/ نانوكربون من سعف النخل بطرائق بسيطة عن طريق الانحلال الحراري والطحن باستخدام الكرات. تدعم التوصيفات التركيبية الكيميائية والمورفولوجية تكون جزيئات الكربون ذات الحجم شبه النانوي. أستخدم الكربون المحضر لتطبيقات استشعار مركبات الفينول كهروكيميائياً وتطبيقات المكثف ذو السعة الفائقة بنجاح. استخدام الكربون المحضر كمادة للقطب الكهربائي بعد التثبيت على قطب الكربون الزجاجي لتصنيع مستشعر كهروكيميائي للكشف عن مادة ١- نفتول و 2- نفتول بشكل متزامن. ووفرت الدراسة طريقتين لاستخدام المستشعر الكهروكيميائي. تعتمد الطريقة الأولى على الأكسدة المباشرة لـ ١- نفتول و 2- نفتول. بينما تعتمد الطريقة الثانية على قمم الأكسدة والاختزال لتكوين الكينون من ثنائي هيدروكسي النفثالين المتولد. تُظهر الطريقة الثانية أداءً تحليليًا أعلى تجاه الكشف المتزامن لـ ١- نفتول و 2- نفتول بالمقارنةً بالطريقة الأولى. وفي جزء آخر من العمل، تم استخدام الكربون المحضر كمادة للقطب الكهربائي حيث تم تثبيت الكربون على ركيزة فولاذية (مجمع التيار) لتصنيع مكثف ذو سعة فائقة عالي الأداء. استفاد المكثف الفائق المُصنَّع من سلوك السعة الكهربائية للطبقة المزدوجة للكربون وسلوك السعة للذرات المتغايرة الموجودة في الكربون. ويوفر جهاز المكثف ذو السعة الفائقة المطوّر شحنًا / تفريغًا كبيرًا باستخدام الكهرل الأمثل (0.1 م من حمض الكبريت)

وينتج سعة عالية محددة تبلغ (~ 107 فاردا / ج) ويتم الحفاظ عليها فوق 92٪ من السعة الأولية بعد 1000 دورة شحن/ تفريغ. علاوة على ذلك، يوفر المكثف ذو السعة الفائقة كثافة طاقة تبلغ حوالي 10 واط / كج بكثافة طاقة تبلغ 200 واط / كج تقريبًا. يوفر هذا العمل مكثفًا فائقًا غير مكلف وعالي الأداء ويعتمد على الكتلة الحيوية (سعف النخل) وهذا يرشحه ليكون مناسبًا لتصنيع بكميات كبيرة في المستقبل. علاوة على ذلك، تم دعم العمل بجزء إضافي وهو تصنيع جهاز مكثف ذو سعة فائقة متماثل يعتمد على شبكة فولاذية مدعمة بترسيب بوليمير انيلين عليها كهربائيًا. نظرًا لقدرتها على التوصيل الفعال ، والطبيعة المسامية، والتكلفة المنخفضة، فإن الشبكة الفولاذية تعد خيارًا جيدًا كمجمع تيار لتصنيع مكثف ذو سعة فائقة عالي الأداء بتكلفة منخفضة. المكثف الفائق المصنَّع له سعة نوعية عالية تبلغ (~ 353 ملي فاراد ل سم²). علاوة على ذلك، المكثف ذو السعة الفائقة قادر على توفير كثافة طاقة ساعية تبلغ 26.4 ميكروواط ساعي ل سم² بكثافة طاقة تبلغ 400 ميكرو واط ل سم². يُظهر المكثف الفائق المصنَّع ثباتًا عاليًا، حيث احتفظت السعة الأولية كما هي تقريبًا بعد 1000 دورة شحن / تفريغ. بشكل عام ، يمكن أن تكون الشبكة الفولاذية المعدلة بوليمر انيلين مرشحًا واعدًا للإنتاج على مستوى ضخم وللتطبيقات الواسعة نظرًا لتكلفتها المنخفضة وأدائها العالي.

CHAPTER 1

INTRODUCTION

During the last few decades, the population of the world and urbanization level have been rising dramatically which increases the environmental pollution and demand of energy. To control environmental pollution, the detection of environmental pollutants is very important. Besides, the development of good performance energy storage devices is essential for proper utilization of energy including renewable energy to meet the rising demand of energy.

These days, monitoring the environmental pollutants is an urgent requirement to protect human life. This monitoring requires development of highly sensitive and selective sensors for different sorts of environment pollutants such as phenolic compounds [1]. Although these compounds (e.g. p-cresol, 3-ethylphenol, and 3,4-dimethylphenol) can be found in different natural food sources such as vegetables and fruits [2], most of the phenolic compounds are considered as hazardous pollutants for their harmful effects on the human body and health. In addition, these compounds are used widely in industry like dye, pharmaceutical, petroleum and food industries in different forms as a reactant, product or waste [3-5]. It indicates that there is a high chance to expose phenolic compounds to the environment. This gives a high priority to the detection of these compounds in different types of samples including water, food, petroleum, soil, and industrial samples. The common methods of the phenolic compound detection are the chromatography and spectrophotometric techniques which are time-consuming, high-

cost, and require professional trainers and staff and a large space for the instruments [6-9]. These methods in general could not be used in-situ or in-vivo and onsite analysis which limits the detection conditions. Furthermore, these techniques could use toxic reagents such as methanol, dimethyl formaldehyde etc. which cause harm for the environment and for the employers. For all these reasons, it is essential to find alternative methods in future which could solve all these problems and develop the analysis process. Electroanalytical chemistry is considered one of the promising areas for solving this challenge. This is due to its advantages like the short time determination portable, onsite analysis, low-cost, environmentally friendly, using small amounts of the solvents and materials. It could also provide us with the in-situ and in-vivo analysis in some cases and the possibility of being used by general and non-professional people [10-12].

Starting with electrochemical sensing, the electrochemical sensor is a device to detect an analyte in the matrix. In three-electrode system, the working electrode is a recognition strip of the target analyte. The working electrode, reference, and counter electrodes are used with a potentiostat to generate a signal for analyte [13].

Secondly, to fulfill the demand of electricity, the energy storage device is one of essential components as energy generating or harvesting. The supercapacitor is an energy storage device with a capacitance value much higher than other capacitors. Supercapacitor can be divided into two main types: electrostatic absorption and desorption called as a double layer capacitor - EDLC and a redox reaction capacitor or called also pseudocapacitor [14]. Compared with batteries, supercapacitor has a higher power density and a higher recharging rate in addition to more charge and discharge cycles. In addition of these advantages, it offers superior low temperature performance, long service and life, high

reliability of performance, reducing the size and the cost compared to the battery, and meet the green chemistry requirements make it a good eco-friendly device. However, science is going on for further development of supercapacitor to make it more meaningful in terms of low cost and high performances [15, 16].

It is noted that the performance and cost of the electrochemical sensor and supercapacitor significantly depends on the electrode materials. Generally, gold [17, 18], platinum [19], and glassy carbon electrodes [20] are commonly employed working electrodes for sensor fabrication. However, their poor electrochemical properties toward most of the analytes or high cost limits their practical applications. To increase properties, the surface modification of the substrate electrode materials with nano/micro-structured electrocatalyst is a common strategy [21]. The uses of carbon nanotube (CNT) [22], graphene [23], gold nanoparticle [24], platinum nanoparticle [25] as electrocatalysts are very common. Besides, graphene and CNT is also very popular as electrode materials [26]. It is remarkable that in Middle East including Saudi Arabia, the palm tree rising occupied a huge sector of the agriculture and food industry [27]. Consequently, there is a huge amount of date palm-based biomass including leaves, trunks, stones which could use in synthesis of carbon materials for low cost and useful device fabrication including electrochemical sensors and supercapacitor [28, 29].

One of our group, recently prepared a nano/micro carbon from date leaves via pyrolysis and ball milling for oil enhance recovery (OER) application [30]. However, this has not applied for any other application including sensor and supercapacitor fabrication. To make this locally produced date leaves-derived nano/microcarbon more popular, there are requirements for further research to apply it in multiple research fields like sensor and

energy storage. This inspired us to use the date leaves derived nano/micro carbon for fabrication of an electrochemical sensor of simultaneous detection of phenolic compounds and high-performance supercapacitor.

1.1 Supercapacitors

Researchers have been motivated to investigate various renewable energy sources due to the finite availability of fossil fuels and the long-term damaging impacts of greenhouse emissions. It is necessary to develop energy conversion and storage technologies in order to overcome the obstacle related to renewable energy that comes from solar and wind sources. This obstacle prevents the full exploitation of the abundant renewable energy that can be generated from these resources. Several electrical energy storage technologies have been used in this setting, allowing efficient power storage, rectification, transportation, and delivery [31-33]. Such energy storage technologies as batteries and fuel cells have served quite close to our daily lives. Still, others, including flywheels, compressed air, pumped hydro, superconducting magnets, and supercapacitors, are crucial from the industrial point of view. Batteries have been widely employed of various sizes because of their exceptional performances, yet, they have several drawbacks like low power density, safety concerns, heat generation, and limited cyclic life [34-36]. Therefore, developing a durable, small, and secure energy storage device with high electrochemical performance would surely revolutionize the design of electric energy generation, distribution, and utility for industry and the military [31, 32, 35-42].

Capacitance, energy, and power densities are the three fundamental concepts that are utilized in the process of characterizing the effectiveness of supercapacitors. The device's capacitance measures a device's capacity to hold an electric charge. The capacity of an

object to store an electric charge proportional to its mass is referred to as the substance's specific capacitance. The cyclic voltammetry (CV) method and the galvanostatic charge discharge process are typically utilized to obtain information about the type of supercapacitors [35, 36, 40-44]. Different underlying phenomena can lead to different types of supercapacitors. The mechanism of the ion store is broken down into the following categories. Electric double-layer supercapacitors (EDLCs) are supercapacitors that store energy by accumulating an electrostatic charge at the electrode/electrolyte interface (EEI), where ions are physically adsorbed and desorbed, storing energy [45-50]. Figure 1.1 shows that the cyclic voltammetry of faradic reactions does not participate in the energy storage process of EDLCs. Carbonaceous materials like activated carbon are commonly used in EDLCs. The EDLCs have a higher power density than pseudocapacitors.

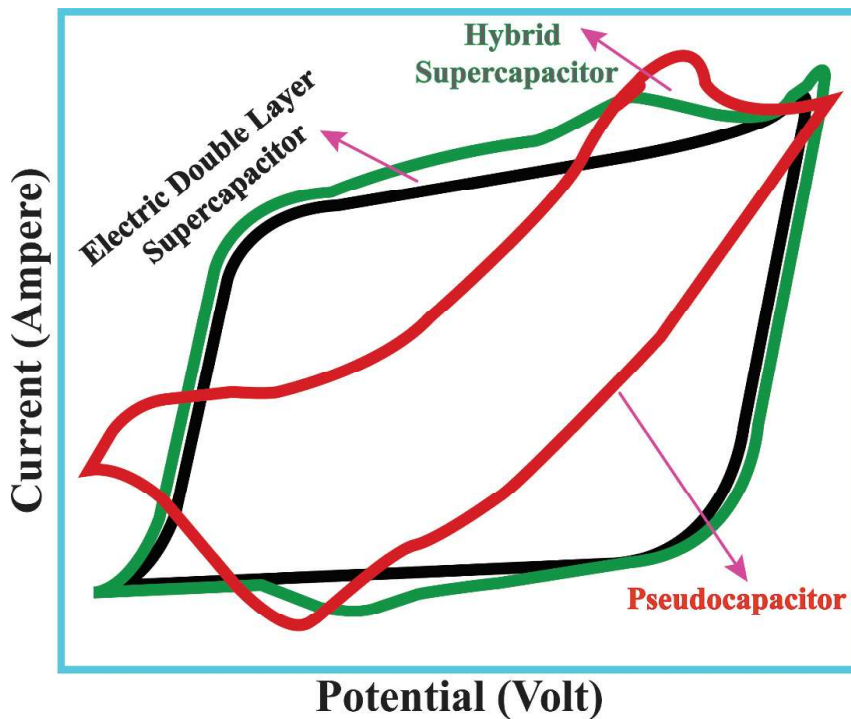


Figure 1.1. Supercapacitor classification based on cyclic voltammetry.

They are extremely rapid in terms of charging and discharging, but their low energy density remains an issue. Pseudocapacitors are supercapacitors that store energy through reversible redox reactions (Faradaic reactions). The faradic reaction occurs at the electrode surfaces. The faradaic reactions have oxidation and reduction peaks, which are depicted in (Figure 1.1) as upper and lower peaks, respectively. Pseudocapacitors outperform EDLCs in terms of specific capacitance and energy density. These are often made up of oxides, sulfides, and conductive polymers. Hybrid supercapacitors are those that have properties of both EDLCs and pseudocapacitors [51-53]. Such supercapacitors use faradaic and non-faradaic reactions for charge storage. These retain both high energy density and power density at the same time. Their cyclic voltammetry curve differs somewhat from the rectangular shape of EDLCs and has a little hump, as seen in (Figure 1.1).

There are various approaches where supercapacitors can be divided into different types, i.e., depending on charge storage mechanism, assembly of electrodes, and size & shapes.

1.1.1 Classification supercapacitors based on charge storage mechanisms

Supercapacitors are classified into three types based on their working principle of charge storage, i.e., EDLC, pseudocapacitor, and hybrid supercapacitor.

EDLCs

EDLCs are a type of supercapacitor that stores energy through the gathering the charges at the EEI [54-56]. Activated carbon, graphene, and carbon nanofibers are examples of carbonaceous nanomaterials typically used to construct the electrodes of EDLCs. These materials have a big specific surface area and a wide range of pore sizes [35, 42, 43, 57,

58]. Because carbon materials have a hierarchical porosity, the diffusion of electrolyte ions to the surfaces will be speeded up, especially at higher scan rates/current densities. Consequently, it is essential to exercise control over both the pore size and the pore size distribution of the electrode materials, which substantially impact the supercapacitors. To build carbon materials with regulated surface chemistry, interconnected pore structures, small pore size distributions (that are susceptible to electrolyte ion diffusion), and short pore lengths are required [35, 41, 49, 59-61]. The Helmholtz double-layer model provides an explanation for the energy storage process of an EDLC. According to this model, the two oppositely charged layers that arise at the EEI are split by small gaps (usually atomic level), as demonstrated in (Figure 1.2). Within the Stern layer, the term "inner-Helmholtz plane" refers to the highly adsorbed ions that are produced by the electrode. A known as the outer-Helmholtz plane comprises particularly adsorbed ions as well as counter ions that are not specifically adsorbed at the EEI [62, 63]. Because of the mechanism through which they store electrostatic charge, EDLCs do not undergo a Faradaic redox reaction, and a rectangular pattern characterizes the behavior of their CV curves [64].

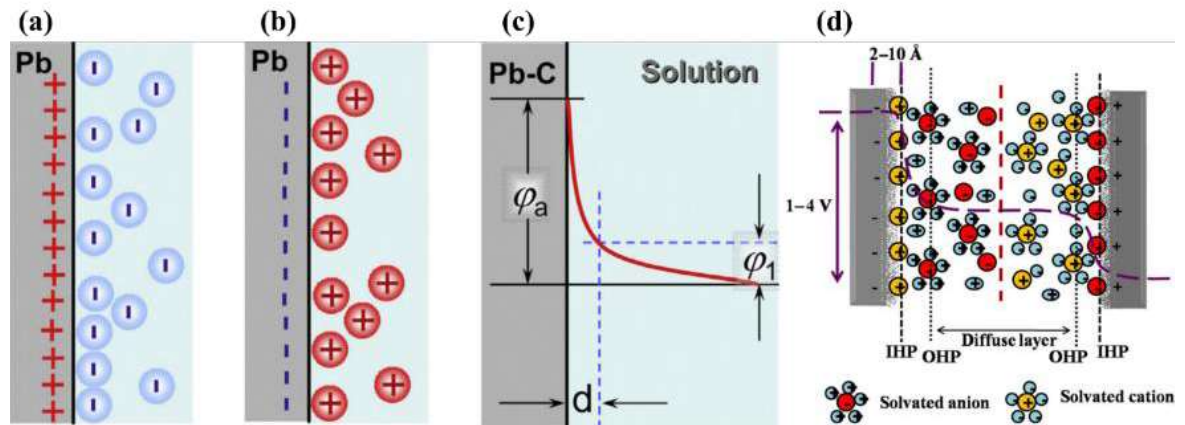
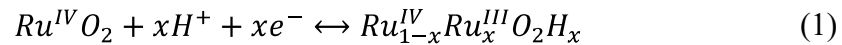


Figure 1.2. EDLCs potential and charge distributions at the EEI of (a) positive electrode, (b) negative electrode, and (c) Helmholtz double layer processing reproduced with

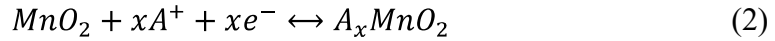
permission[65]. Copyright 2013, Elsevier. (d) Stern model at the EEI, and diffused layer. Reproduced with permission[66]. Copyright 2018, Elsevier.

Pseudocapacitors

Pseudocapacitors have electrodes made of redox-active nanomaterials, which are typically transition metals-based materials and conducting polymers. The electrical energy is stored in the rapidly reversible faradaic redox processes that take place at the electrode surface [35, 67-69]. Pseudocapacitors have a relatively high energy density, but because of the quick redox reactions that occur during the charging and discharging processes, they also accumulate irreversible components. Consequently, this results in a decline in cyclic stability performance [64, 67]. The pseudocapacitor electrode materials go through fast reversible Faradaic redox processes, resulting in the Faradaic current being conducted via the supercapacitor device. Oxidation and reduction peaks are involved in the faradic process. The process of charging and discharging batteries is analogous to the behavior of this mechanism. Since 1971, researchers have investigated a wide selection of pseudocapacitive materials of metal oxides. The first evidence of the pseudocapacitance of RuO₂ in a supercapacitor was found and published by Trasatti et al [70]. When subjected to electrochemical cycling in aqueous electrolytes of elevated pH values, RuO₂ demonstrates the properties of pseudocapacitance. It is generally accepted that the pseudocapacitive behavior of RuO₂ may be traced back to a chain of reversible reactions, one of which is the transfer of electrons at the electrode surface (represented by equation (1) [71].



Furthermore, several known transition metal-based materials, such as MnO_2 and Fe_3O_4 , also exhibit core Faradaic reactions. Because of their many valence states outperform EDLCs in initiating fast oxidation and reduction reactions at surface. This allows them to store a substantially greater amount of energy at a much faster pace during charge and discharge. As an illustration, it is shown in equation (2) that surface and bulk redox processes in MnO_2 can store charges between the +4 and +3 manganese oxidation states [72]. Where, A describes an alkaline cation (i.e., Li^+ , Na^+ , and K^+).



This type of supercapacitor has fast surface redox or intercalation processes and a double-layer capacitance to increase energy density while keeping EDLC-like fast timings for charging and discharging [73]. In 1991, the term pseudocapacitance was coined by Conway et al [74]. EDLCs and batteries are two extremes of the energy storage spectrum. Pseudocapacitance energy storage, however, comes somewhere in the middle. There are three pseudocapacitance types: the surface Faradaic reaction, the intercalation, and the monolayer adhesion, as shown in (Figure 1.3). A monolayer adsorption happens when two metals with different redox potentials come together to create an adsorbent layer (this is called underpotential deposition). Underpotential lead (Pb) depositions on gold (Au) electrodes are well-known examples [75]. Due to the increased contact between Au and Pb in crystal-like Pb metal, it is easier for Pb to be deposited onto Au than it is for Pb to be deposited onto itself. Surface Faradaic redox pseudocapacitance on the electrode materials results from charge-transfer mechanisms that adsorb alkali ions onto or near the electrode surface. Pseudocapacitance is a phenomenon that can occur when the intercalation is not restricted to diffusion, that occurs when ions migrate slowly through

the structure of electrode materials. Bulk intercalation pseudocapacitance takes the place of surface redox pseudocapacitance, which is unique to the electrode surface or the area immediately adjacent to it [76].

Hybrid supercapacitors

Furthermore, another technique has been implemented to integrate both the mechanisms of charge storage for pseudocapacitors and EDLCs to build an efficient device that could emulate the excellent energy density of pseudocapacitors. These high-performance devices are referred to as hybrid supercapacitors, and they are able to sustain high energy and power densities concurrently [77, 78]. Instead of using carbon, transition metal-based materials, and conducting polymers individually, scientists prepared hybrid composites of these active materials for hybrid supercapacitors. These hybrid composites are inexpensive, chemically stable, mechanically flexible, and demonstrate excellent electrical conductivity. To govern the hybrid supercapacitors energy storage principle, EDLCs and pseudocapacitors are connected (Figure 1.3(f)). Because pseudocapacitors lack the limiting property of EDLCs, and vice versa, the combination of these two components allows the restrictions of the combining components to be concealed, which results in an increase in capacitance. Hybrid supercapacitors can either be symmetric (shown in Figure 1.3(g)) or asymmetric (shown in Figure 1.3(h)), and this depends on the architecture of the assembly. The electrochemical behavior is better when hybrid supercapacitors are created from independent electrodes made of dissimilar materials than when the electrodes are used independently. Both cyclic stability and affordability, two key variables in determining whether pseudocapacitors would be successful, are preserved in hybrid systems. Because of its higher specific capacitance values and wider

operating potential windows than symmetrical EDLCs, the hybrid type offers a higher energy density than those devices [35, 36, 49, 61, 79]. The CV curves of hybrid supercapacitors have some oxidation/reduction peaks, which are shown as minor bumps in (Figure 1.1). This is a little departure from the rectangular shape of EDLCs' CV curves. Hybrid supercapacitors are regarded as a potential game changer for future energy storage systems development. They have developed as an alternative to electrochemical energy storage systems with the aim of achieving higher energy density demand. The performance of supercapacitors depends on the materials that make up their electrodes when it comes to practical applications. The hybrid supercapacitors have high capacitance, greater power, and excellent energy than the pseudocapacitors and EDLCs that are already on the market. This is due to the fact that the hybrid supercapacitors utilize two distinct charge-storing processes. In most cases, the asymmetric method performs the function of an amplifier in the respective capacitance values. The asymmetric hybrid supercapacitors are made up of a positive electrode that contains redox-active materials and a negative electrode that is created by combining a carbon material with an electrolyte and a separator in between. The counter electrolyte ions migrate towards both the anode and cathode throughout the process of charging or discharging. EDLC behavior is provided by attracting or releasing the ions on the surface, while pseudocapacitive behavior is caused by fast reactions at the anode caused by negative electrolyte ions. The pores and the materials area are the key for energy efficient hybrid supercapacitors. These factors make the ions accessibility and boost the capacitance. In a similar vein, the ability to tune the morphology of the electrode material for hybrid supercapacitors has been considered to be another crucial aspect. Careful

morphological adjustment of the nanostructures changes the unique properties of nanomaterials. It exposes active sites and distinct crystal facets, both of which can frequently considerably impact the hybrid supercapacitors electrochemical performances [60, 80, 81].

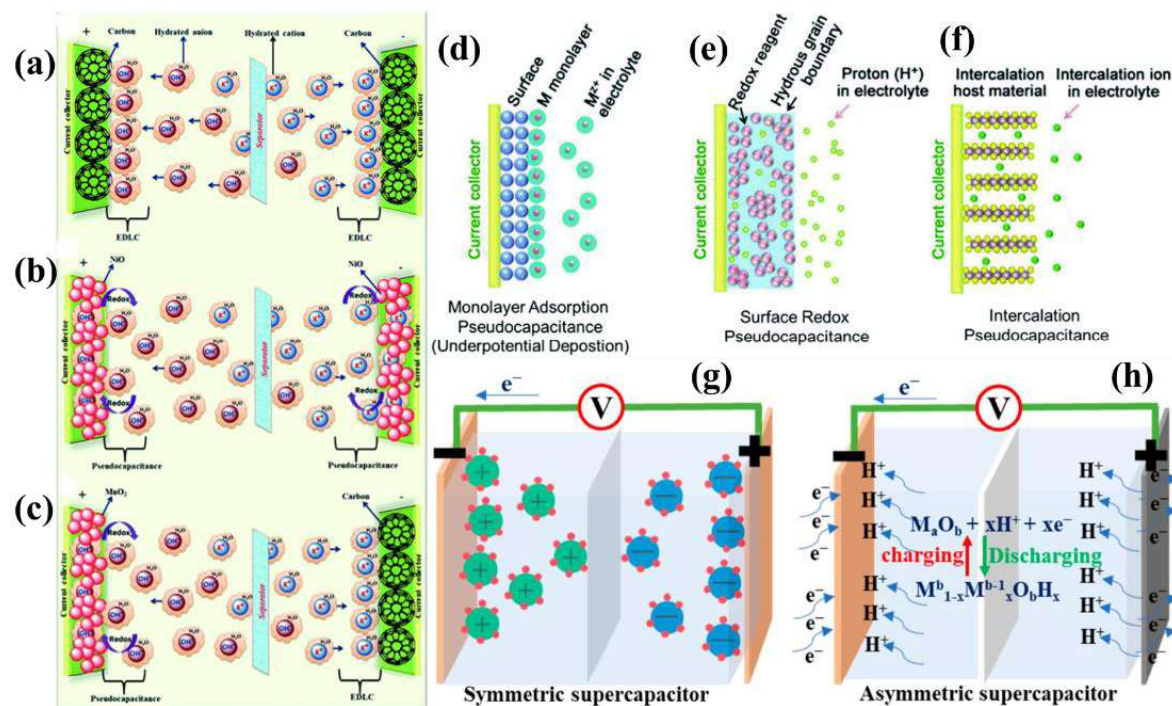


Figure 1.3. (a) EDLCs, (b) pseudocapacitors, and (c) hybrid supercapacitors charge storage mechanisms. Reproduced with permission.[82] Reproduced under the terms of the CC BY-NC 3.0 license. Copyrights 2019, Pal et al. (d-f) Various pseudocapacitance methods. Reproduced with permission.[83] Reproduced under the terms of the CC BY-NC 3.0 license. Copyrights 2019, Huang et al. (g, h) Symmetric/asymmetric hybrid supercapacitors. Reproduced with permission.[84] Reproduced under the terms of the CC BY 4.0 license. Copyrights 2022, Zhang et al.

1.1.2 Supercapacitor types based on electrodes configuration



Figure 1.4. Schematics for the symmetric and asymmetric configuration of supercapacitors.

Depending on the type of electrodes, a supercapacitor can have two configurations, i.e., symmetric, and asymmetric. A symmetric supercapacitor is made up of positive and negative electrodes of the same material, which is typically carbon. In contrast, as illustrated in (Figure 1.4), an asymmetric supercapacitor can have a variety of electrode material combinations[85]. The electrodes of a symmetric device have identical active

materials and the same mass loading ($m_+ = m_-$). EDLC-based materials or materials with EDLC and Faradaic capacitance contributions are typically used to fabricate symmetric supercapacitors. Only using Faradaic materials results in symmetric supercapacitors that are rarely used because redox reactions only occur at either positive or negative voltages[86]. Within the same electrolyte, asymmetric supercapacitors combine two distinct types of active electrode materials, one of which is EDLC and the other of which is pseudocapacitive. Asymmetric supercapacitors are another name for supercapacitors that have the same kind of active electrode material on each electrode (Figure 1.4).

1.1.3 Supercapacitor types based on device configuration

In addition to the material itself, the performance of a supercapacitor cell can be significantly altered by several factors relating to the processing conditions of the electrodes and the cell assembly. These factors include electrode thickness and density, cell pressure, and the pre-conditioning process. The production of a supercapacitor only requires a few steps, including the preparation of a homogeneous mixture of components, the creation of an electrode layer on a current collector sheet, the assembly of the cells, and the packaging of the finished product.

1.2 Electrochemical sensor

An electrochemical sensor is an electrochemical device that specifically detects one or more chemical analytes in a matrix [87]. The process of electrochemical sensing consists of many steps that lead to the final readable outcome (Figure 1.5) and (Figure 1.6, b). The process starts with detecting the target analyte using a specific chemical reaction or recognition method [60, 87]. The analyte detection occurs on a chemical surface called a receptor which catalyzes the detection of a chemical reaction or provides the recognition

principle required for detection [60]. Using a transducer, the chemical signal is translated into an electric signal. The produced electric signal is transferred into a readable signal using a processor [60]. At this level, the final readable readout signal could be generated on a computer or any electronic device [60].

The electrochemical sensors have many advantages, including sensitivity, accuracy, occasionally, quick information and data collection, in-vivo and on-situ application, determination without previous separation requirements, easy use, and low cost. Consequently, electrochemical sensors have attracted many scientists and researchers for the last three decades [88, 89]. The applications of electrochemical sensors vary to cover many life sectors, including the health [90], environmental [91], and industrial [92] sectors. In the health sector, electrochemical sensors could be used to detect chemicals or biochemicals in the case of electrochemical biosensors [93]. The detection could be done through human liquids, including blood [94], saliva [95], urine [96], and sweat [97]. The usage involves cancer diagnosis [98], DNA and RNA diagnosis [99], heart diseases [100], alcohol and glucose monitoring [101, 102], and overall health monitoring [103]. In the environmental sector, pollutant detection plays a major role in pollution control [104]. Accordingly, electrochemical sensors meet the requirements for quick in-vivo and in-situ detection of pollutants [105, 106]. Electrochemical sensors could be used to detect pollutants contamination in soil [107], air [108], and water [105]. This, in turn, spotlights the importance of electrochemical sensors for urgent water detection as it is a vital source for human life[105]. In the industrial sector, quick in-situ detection plays an essential role in improving the industry process and enhancing product performance [109]. As a result,

electrochemical sensors represent the suitable tools to monitor the industrial process and achieve the quick required quality control [109-111].

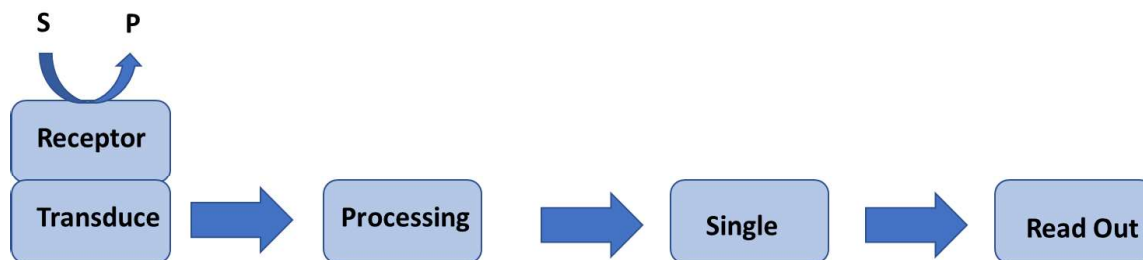


Figure 1.5. Electrochemical sensor processing.

Electrochemical methods are considered the key to understanding electrochemical sensor mechanisms [60]. The electrochemical methods could be classified into many categories due to the way of reaction with the analyte in the matrix. This includes two categories which are solution and interference methods [60]. The electrochemical solution methods are based on conductometry (Figure 1.6) [60]. Conductometric measurement depends on measuring the change in the conductivity of an electrode surface due to the change in the analyte concentration [60, 112]. While the interference methods could be divided into two categories which are static and dynamic electrochemical methods. The static method could be identified simply as measuring the electrode surface potential in the case of a current equal to zero. The potentiometry is scheduled as a static method and depends on measuring the potential between two electrodes by applying a high-impedance voltmeter [60, 112]. On the other hand, dynamic electrochemical methods depend on the electron transfer between the electrode surface and the target analyte. The dynamic methods are divided into controlled-potential methods, including voltammetry, amperometry, and coulometry, and controlled current methods in coulometric titrations [60, 112].

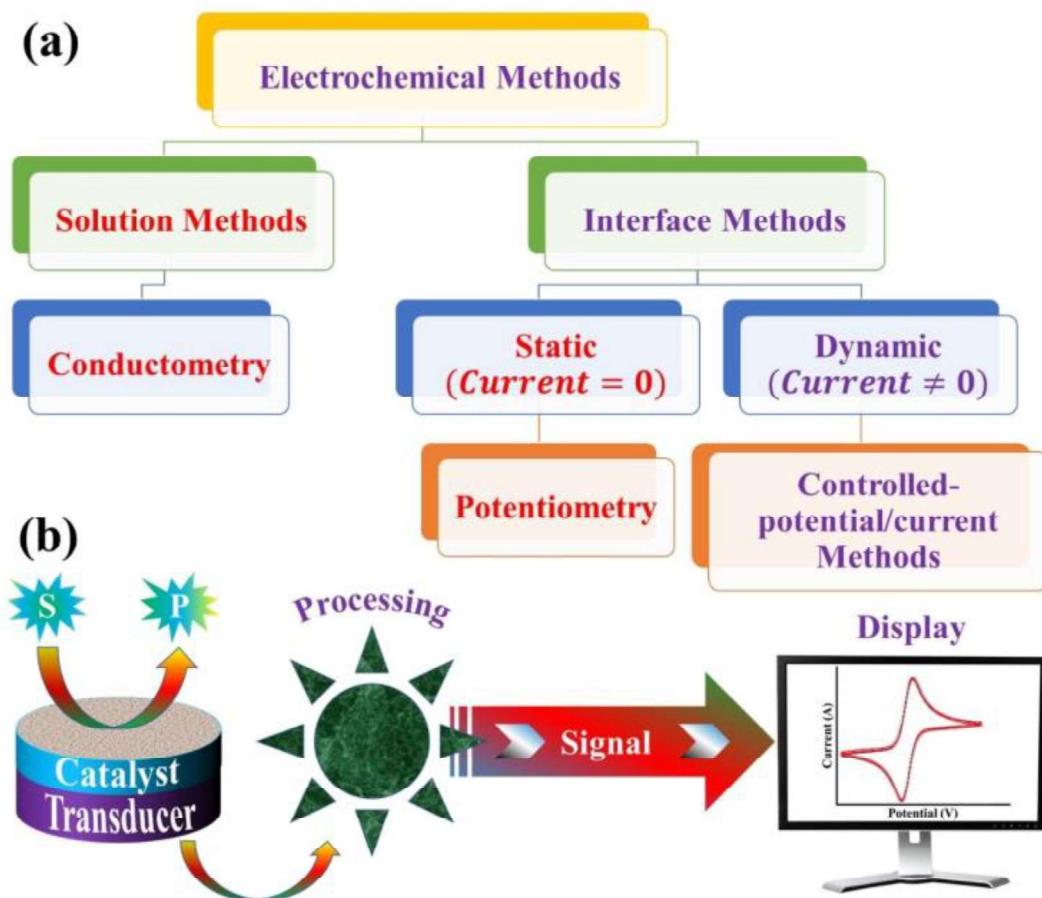


Figure 1.6. (a) The electrochemical methods classification, (b) the electrochemical sensor processing reproduced with permission[60]. copyright 2021, Wiley

The selectivity and sensitivity of the electrochemical sensor are considered the core of the detection process [113, 114]. These two characteristics are functioned by the sensing part of the electrochemical sensor, which transfers the chemical information in the sample into the sensing signal. As a result, the sensing part is considered the core of the electrochemical sensor. The sensing part of the electrochemical sensor consists of the electrodes and the cell, which provide the space for the sample and the electrolyte in contact with the electrodes [115]. In general, the electrochemical process requires at least two electrodes which are the working and reference electrodes. Most electrochemical

measurements could require three electrodes: working, reference, and counter. The measurement of voltage takes place between the working and reference electrodes [115, 116]. While the measurement of current takes place between the working and counter electrodes. The working electrode is the heart of the sensing process, where the electrode material plays the basic role of catalyzing the electrochemical reaction with the analyte. the electrochemical reaction of the analyte should be specific to the analyte and could be an electro-oxidation or electro-reduction [115]. The electrochemical reaction has two essential data: the potential and current of the electrochemical oxidation or reduction peak. The qualification and quantification analyses could be determined based on the electrochemical peak's potential and current [115]. The improvement of the electrochemical sensor performance depends on the properties and characteristics of the electrode material in the working electrode. The electro-catalytic properties of the electrode material determine the possibility and the value of the required potential of the electrochemical reaction. While the surface area of the material determines the quantity of the analyte that could be reacted on the electrode surface. This, in turn, governs the quantitation analytical performance of the electrochemical sensor [115]. Consequently, preparing an electrode material with a high surface area is desirable to enhance the electrochemical analytical performance. Synthesis of a nano-scale material is an effective method that provides a high surface area. Furthermore, the chemical composition of the electrode material is considered the critical factor in determining the catalytic behavior of the electrode. This requires preparing an electrode material with a specific chemical composition by using a composite or depending on the synthesis process and the primarily used material in the first place.

CHAPTER 2

LITERATURE REVIEW

Different techniques were used to detect different phenolic compounds including liquid and gas chromatography [117], spectrophotometry [118], molecular imprinting [119], fluorimetry [120, 121], Fluorescence [122], enzyme-linked immunosorbent assay [123].

Electroanalytical methods are considered conventional methods for analysis due to their advantages including simplicity, selectivity, sensitivity, moderate cost, and ability to miniaturization [124-126]. The analytical electrochemical detection was used to detect the phenolic compound in order to minimize the detection device and obtain all the benefits of electrochemical analysis. Different types of electrodes like gold [127], Pt [128], glassy carbon electrode (GCE) [129], have been employed to detect various phenolic compounds. Different types of conventional carbon electrodes were tested to detect phenolic compound like carbon print electrode [130], pencil electrode (PE) [131]. Nano-carbon material electrodes have a huge improvement to enhance the electrode analytical performance due to their properties including enhancement of the thermal-resistance, conductivity, active surface, and catalytic properties [132]. As example, multi-walled carbon nanotubes (MWCNT) were studied for highly electrochemical analytic performance towards phenolic compounds [133]. Furthermore, carbon nanotubes (CNT) is investigated towards phenolic detection improving the conductivity, chemical stability, and large specific area [134]. Carbon derived from Palm date biomass were tested recently to fabricated electrodes to detect just hydroquinone [135] and catechol [136] individually.

The other important trend towards the phenolic compounds detection is simultaneous detection of more than one compound as many of them are coexisted in the naturals and different samples like the isomers of 1-naphtol and 2-naphthol [137]. Many research were done to detect different phenols compounds simultaneously. 1-naphthol and 2-naphthol are an important phenolic compounds to detect simultaneously due to being isomers in the first place, and due to its highly hazards on the environment and human health. 1-naphthol is considered hazardous due to its genotoxicity, protein toxicity and ability to decrease the semen quality and testosterone levels in the human [138, 139]. 2-Naphtol which considered more harmful of 1-naphthol is able to create different systemic intoxications and affect blood circulation causing harm to kidney and liver organs [140, 141]. As it is predictable, Chromatography techniques were used widely for simultaneous detection of 1-naphthol and 2-naphthol [141, 142]. Many types of electrodes and materials were used to for simultaneous electro-detection like nitrogen and phosphorus co-doped porous carbon [137], boron-doped diamond electrode [143], Poly (acridine orange) [144]. Finally, fabrication of a novel simultaneous detection of 1-naphthol and 2-naphtol sensor from biomass derived nano-carbon is an importance due to the low cost and being environmentally friendly. Furthermore, it must be highly sensitive which will be fabricated in our work and achieved the other properties. In addition of advantage of that the biomass is the date palm leaves which is a local agriculture waste in Saudi Arabia.

On the other hand, due to the importance of energy storage, Supercapacitor is an ideal tool to store energy. The supercapcitor has many advantages including high energy storage, quick charging time, maximum life cycle, extremely low internal resistance, and

eco-friendly [145-147]. However, more research is required to improve its performances and lowering the cost for wide application [148].

Improving the performance of supercapacitors and lowering the cost depends on the material that will be used in the first place [149]. Furthermore, being environmental friendly, low-cost are essential properties in material to reach the green chemistry and current industrial economic requirements [150, 151]. Different types of materials were used for supercapacitors' electrodes like oxides, polymers, and carbon and nano carbon materials. Based on their properties, different type of carbon materials is widely used in double layer supercapacitors [152] like graphene [153], graphite [154], nanotubes (CNTs) [155] carbon fibers [156], and biomass carbon [157]. The biomass carbon was obtained from different kinds of plants and plants waste including fruits [158], cherry stones [159], leaves of tall palm [160], *Syzygium cummini* [161], *Albizia procera* leaves [79], and waste of tea leaves plants [162]. To obtain the biomass carbon, many treatments are required including the heat treatment and carbon activation [163]. With comparison of porous-nanostructured carbon (NSC) [164], the pyrolysis treatment carbon from biomass gave a better stability and superior capacitance [165].

Palm date derived carbon is used for many applications including as an adsorbent material [166], waste water treatment [167], carbon dioxides adsorption [168], removal of phenolic pollutants [169], heavy metals [170] and dyes [171] and in food industry as a filter aid for sunflower oil [172]. In analytical electro chemistry, it used in some detections which are Hydroquinone [173], catechol [173]. Different treatment and processes of preparing nano carbon from different parts of palm tree obtains different types of carbon differ in structures and catalytic and morphological properties [174, 175].

This gives opens the door to more research looking for different types of carbon and the possibility of more applications to apply.

New type of nano/micro carbon derived from palm date leaves was synthesised by our group using pyrolysis and ball milling. In order to fabricate highly sensitive sensor for 1-naphthol and 2-naphthol and highly efficient supercapacitor, this type of carbon will be used and investigate its advantages as a local biomass treatment product, low cost, and environmentally friendly.

CHAPTER 3

Fabrication of high-performance supercapacitor using ball milling date leaves derived carbon

3.1 Introduction

Due to sharp increases in the population and urbanization worldwide, energy demand is increasing. To protect the environment and properly utilize renewable energy, developing energy storage devices using low-cost materials is essential. EDLC stores energy by capturing or releasing the ions, which form a double layer in the area between the electrode material and the solution of electrolyte. While pseudocapacitors depend on reversible redox reactions between the electrode material and electrolyte for charge storage, they are also called faradaic supercapacitors. Hybrid supercapacitors use both the mechanisms of EDLC and pseudocapacitors to store energy [176]. This, in turn, gives the hybrid supercapacitor a high advantage of properties of both supercapacitors of EDLC and pseudocapacitor, which leads to a high specific or areal capacitance, energy density, and power density [177, 178]. According to the fabrication method, supercapacitors can be classified into two categories which are symmetric and asymmetric supercapacitors. Symmetric supercapacitors are composed of similar two electrodes, while the asymmetric is composed of two dissimilar electrodes [178, 179]. Supercapacitors have many advantages, including high power density, quick charging time, maximum life cycle, low internal resistance, and eco-friendly.

Electrode materials like metal oxides, conductive polymers, carbon, and their composites were used for supercapacitor fabrication [56, 180-184].

Palm date-derived carbon is considered one of the useful materials which could be obtained by heat treatment of the Palm trees waste. It is important to mention that the palm tree is considered an important branch of the farming and food industry in many countries worldwide. The palm date-derived carbon is used for many applications, including as an adsorbent material [168], wastewater treatment [185], carbon dioxides adsorption [168], removal of phenolic pollutants [186], heavy metals and dyes [187], and in the food industry as a filter aid for sunflower oil [188]. In analytical electrochemistry, it is used to detect various toxic entities such as hydroquinone [135] and catechol [136]. Different methods of preparing nanocarbon from different parts of palm trees produce different types of carbon which differ in properties such as structures, morphology, size, shape, and electrochemical properties [189]. The date palm-derived-nanocarbon could provide a good active surface area due to its small size. In general, date leaves-derived carbon is prepared by chemical activation, which is complicated to produce on a large scale. However, the door is still open for investigating and developing other preparation methods. Ball-milling is a physical size reducing and a nano-material synthesis method. In addition to its simplicity, the ball milling method requires no chemicals or solvents, which gives it the advantage of being a clean, eco-friendly, and scale-up method. For these reasons, our group used the ball milling method of date leaves-derived carbon, produced by simply pyrolysis of dried date leaves, to obtain low-cost sub-micro and nano-size particles [30]. Due to its unique properties, this ball-milling date leaves derived carbon was used successfully for enhanced oil recovery. It is noted that this ball-milled carbon possesses some heteroatoms like O, Mg, Si, K, Ca, and Zr, which could be beneficial for supercapacitors, including pseudocapacitors [190]. However, nobody used

this prepared nanocarbon for electrochemical energy storage device fabrication, including supercapacitors.

3.2 Experimental

3.2.1 Materials

Sulfuric acid, hydrochloric acid, acetic acid, perchloric acid, nitric acid, and phosphoric acid were obtained from Sigma-Aldrich. Steel strips (304 stainless steel shim) were obtained from a local market in Dammam, Saudi Arabia. The date palm leaves were obtained from local palm farm near King Fahd University, Saudi Arabia. All the equipment and glasses were cleaned and rinsed with distilled water, and the entire used solutions were prepared using deionized (DI) water, which was obtained using water purification. Nitrogen gas (N_2) with high purity was brought from by Specialty Gases Company Limited, Jubail, KSA.

3.2.2 Date leaves derived submicron-nano carbon (DLSNC) preparation

Palm date leaves were washed with detergent, cleaned with DI water, and dried under the sun for a couple of days. Then the leaves were rinsed with water and dried at 110 °C in an oven for one day to eventually remove any trace of moisture. After that, the dried leaves were cut into tiny pieces. The pieces were heat treated using a tube furnace in the nitrogen atmosphere at 850 °C under the conditions of 10 °C/min heating and 5 °C/min cooling rates. The obtained carbon was pulverized to produce soft powder using a blender. Then, a high-energy ball-milling technique was used to mill the final powder to produce the nanocarbon at a speed of 3,000 rpm for 15 hours. Here the zircona balls of

600 μm were employed by maintaining a 1:20 (mass to mass) ratio of carbon to zirconia balls. The preparation of DLSNC is schematically represented in **Scheme 1**.

3.2.3 Fabrication of DLSNC-modified steel (DLSNC/Steel) based supercapacitor

Steel strips were used as current collectors for the supercapacitor electrodes. First, the steel strips (1 cm x 2 cm) were washed with DI water followed by washing with ethanol in ultrasonic bath for 15 minutes each and then dried at room temperature. A DLSNC solution (1 mg/ml) was prepared using DI water with ultrasonication for 30 minutes. 200 μL of the prepared DLSNC solution was dispensed on the steel strip with a dimension of 1x1 cm^2 and was dried at room temperature over 12 hours to obtain the final electrode with a mass of 200 μg of DLSNC.



Figure 3.1. Schematic representation for the DLSNC synthesis and the DLSNC/Steel based symmetric supercapacitor device fabrication.

Then a separator (filter paper) saturated with an aqueous solution of H₂SO₄ (0.1 M) was sandwiched by two of the prepared DLSNC/Steel electrodes (geometrical area 1 cm²) to fabricate the supercapacitor. The fabrication of the DLSNC/Steel-based supercapacitor is shown in (Figure 3.1).

3.2.4 Electrochemical measurements

Different electrochemical tests were done to investigate the developed supercapacitor performance. The tested techniques include cyclic voltammetry (CV), galvanostatic charge/discharge (GCD), and electrochemical impedance spectroscopy (EIS). The measurements of the experiments were performed with an electrochemical workstation (760E-CHI, CH Instruments, Inc., USA). Basic properties of the working electrode materials were also performed using a three-electrode electrochemical system. Here, Ag/AgCl and a platinum wire were used as a reference and counter electrode, respectively.

The specific capacitance was estimated from the CV voltammogram in three electrode system depending on equation 1, while the supercapacitor capacitance using the CV voltammogram of two electrode system was calculated based on equation 2 [191, 192].

$$C_{sp} = \frac{\int I dV}{2 \times m \times v \times \Delta V} \quad (1)$$

$$C_{sp} = \frac{\int I dV}{m \times v \times \Delta V} \quad (2)$$

The C_{sp} represent the specific capacitance measured by the unit of Farad/gram (F/g), $\int I dV$ represents the value of the area under the voltammogram evaluated by the unit of watt (W), m represents the electrode material mass measured by the unit of gram (g), v is

the scan rate measured by unit of V/sec, and ΔV represents discharging potential voltage range measured by the unit of volt (V).

The supercapacitor capacitance was evaluated from the GCD based on equation 3 [192].

$$C_{sp} = \frac{I \times t}{m \times \Delta V} \quad (3)$$

The C_{sp} represents the specific capacitance measured by the unit of Farad/gram (F/g), I represent the discharging current used by the unit of Ampere (A), t represents the discharging time measured by the unit of second (sec), m represents the electrode material mass measured by the unit of (g), and ΔV represents discharging potential voltage range measured by the unit of volt (V).

According to the supercapacitor device performance, other essential values are energy density (E), which was calculated depending on equation 4, and power density (P), which was calculated depending on equation 5 [193].

$$E = \frac{1}{2} \times \frac{C_{sp} \times \Delta V^2 \times 1000}{3600} \quad (4)$$

$$P = \frac{3600 \times E}{\Delta t} \quad (5)$$

E is the energy density measured by the unit of Wh/g, C_{sp} represents the specific capacitance measured by the unit of F/g, ΔV represents the applied potential range measured by the unit of volt (V), P is the power density measured by the unit of W/g, and Δt represents the discharging time measured by the unit of second.

3.3 Results and discussion

3.3.1 Morphological and structural characterization

The prepared DLSNC was investigated using the XRD (Figure 3.2A). The XRD pattern displays the existence of carbon in addition to SiO₂ and ZrO₂ [194, 195]. The XRD peaks at $2\theta = 24.5^\circ$ and 44.4° identify C (002) and C (101), respectively [196]. While the peaks at 2θ angles of 28.2° suggested SiO₂ (101) [197, 198]. The presence of silica in DLSNC is expected due to the plant's source of carbon. In addition, this result was also supported by EDS data in the later discussion. In addition, the peaks at a 2θ angle of 30.5° , 35.1° , 49.8° , and 59.6° represent ZrO₂ (111), (200), (220), and (131), respectively [198, 199]. The presence of ZrO₂ in the Carbon is associated with the milling balls trace from the milling treatment. Next, the DLSNC was examined by FTIR to investigate the presence of functional groups/chemical bonds (Figure 3.2B). The FTIR spectrum represents many peaks, whereas, from the curve, the peaks at 1092 cm^{-1} indicate the presence of a C-O bond and 1723 cm^{-1} and 1458 cm^{-1} suggest the presence of a C=O bond [30]. The presence of a peak at 1583 cm^{-1} displays the presence of C=C. Whilst, the peaks at 2852 cm^{-1} and 2922 cm^{-1} indicate to C-H bond. Finally, the broad peak around 3425 cm^{-1} shows the presence of a hydroxyl group due to moisture [200]. These types of bonds/functional groups in biomass-derived carbon are very common. According to the FTIR, it is clear that the detected chemical bonds indicate a carbon structure which contains SP³ and SP² Carbon, in addition to the existence of the oxygen elements as a ketone and ether bonds and water.

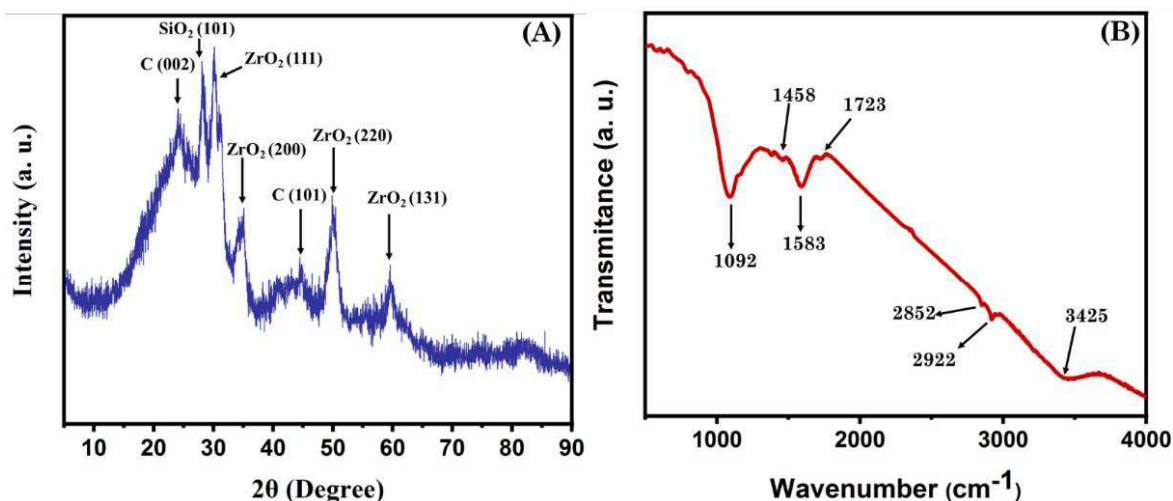


Figure 3.2. (A) XRD pattern and (B) FTIR spectrum of the DLSNC.

The morphological studies of bare steel strip and DLSNC/Steel electrode were done by recording FESEM images (Figure 3.3). Different magnification FESEM micrographs were used to investigate the morphological changes by the modification processes. Steel surface images shown in (Figure 3.3a-c) display a bare smooth surface of the steel. After modification with DLSNC, the surface is covered with carbon particles (Figure 3.3d-f). The surface of the particles is scaly rough with small sharp bumps (Figure 3.3d). This type of surface provides high surface area and improved electrochemical properties. The size of carbon particles varies from 50 nm to 200 nm, which was expected as the ball-milling technique prepared them. This result indicates that ball-milling can reduce the large grains of the carbon, which was prepared by pyrolysis, to such nano-dimensions.

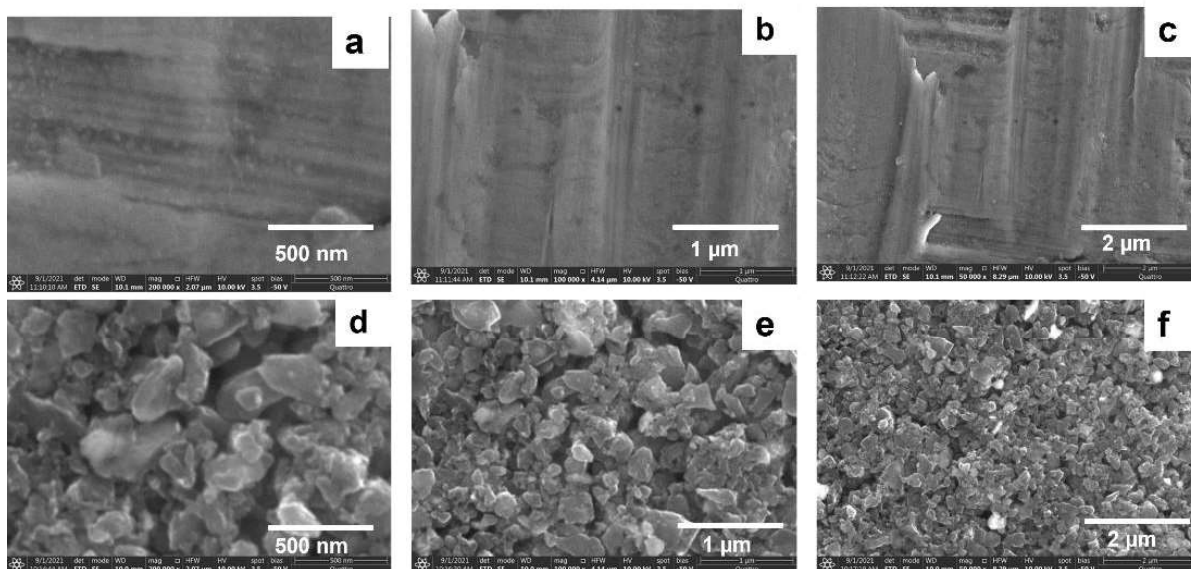


Figure 3.3. FESEM images of (a-c) steel strip and (d-f) DLSNC/Steel electrode.

To investigate the chemical composition of the DLSNC/Steel electrode, EDS and the elemental mapping of the existing elements were recorded (Figure 3.4). According to the EDS spectrum (Figure 3.4a), carbon, oxygen, sulphur, silicon, calcium, and potassium are commonly expected due to their existence in the palm tree leaves composition. On the other hand, the existence of iron, chromium, and the trace of nickel is explained due to the commercial steel strips used as a substrate. The existence of Zr is attributed to the zirconia balls used in the milling process throughout the DLSNC preparation. The elemental mapping images of the DLSNC/Steel show a homogeneous distribution of the elements on the electrode surface (Figure 3.4b-f). The elemental mapping also displays a high-density distribution of C and Fe due to the carbon material composition and steel substrate (Figure 3.4b, g).

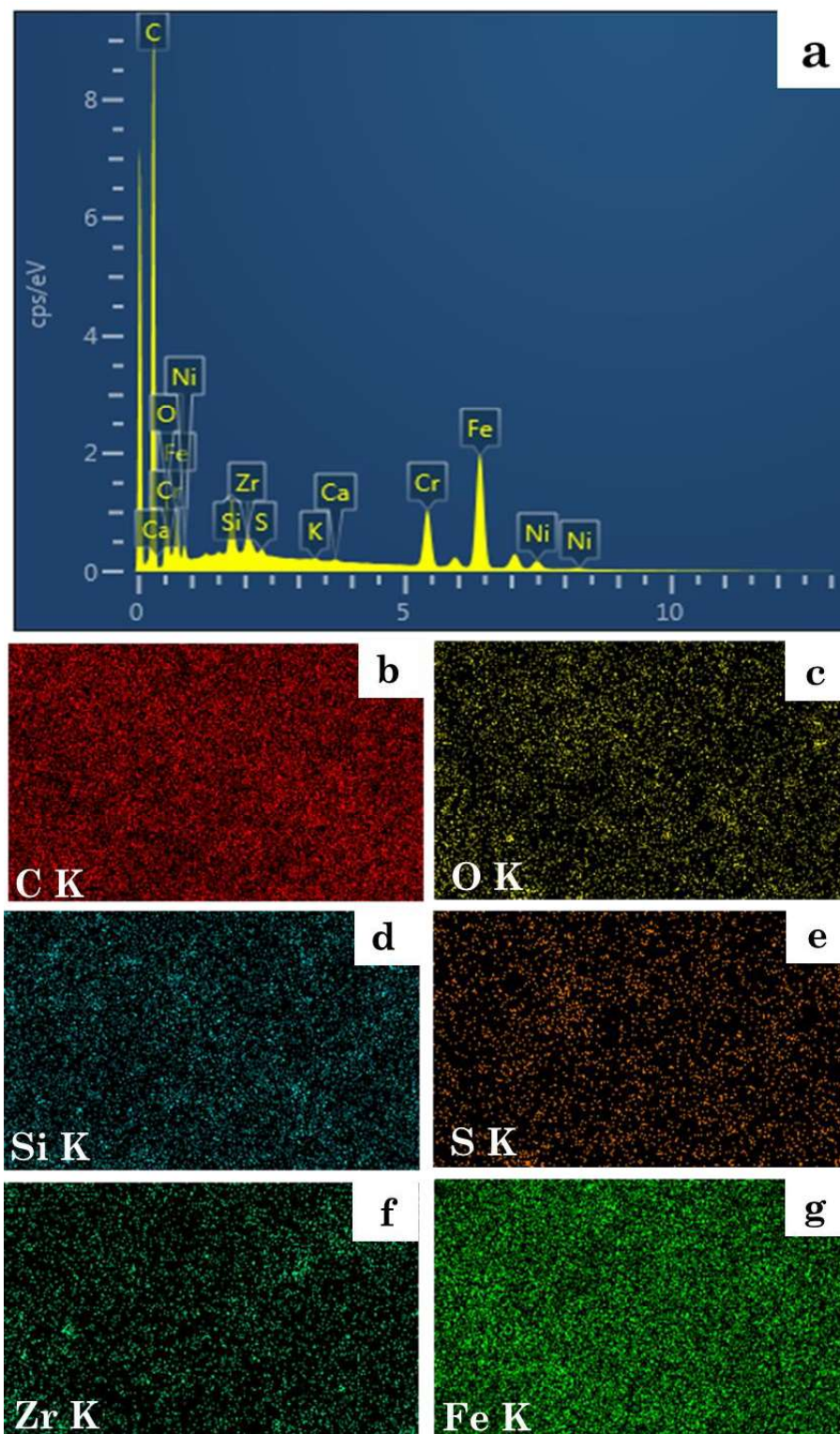


Figure 3.4. (a) EDS spectrum of the DLSNC/Steel and its mapping images.

3.3.2 Electrochemical investigation of DLSNC/Steel toward supercapacitor using a three-electrode system

In the first place, different types of electrolytes were tested using the CV at the same scan rate of 0.05 V/sec (Figure 3.5A). The measurement was done between 0 and 0.8 V (vs. Ag/AgCl), which is selected as a suitable charging/discharging potential window to evaluate the supercapacitor performance of the developed electrodes. The tested electrolytes include sulfuric acid (H_2SO_4), hydrochloric acid (HCl), sulfuric acid (H_3PO_4), perchloric acid (HClO_4), sodium sulfate (Na_2SO_4), and sodium chloride (NaCl). All the electrolytes were prepared as aqueous solutions with a concentration of 0.1 M. In general, the results indicate a dominant EDLC behaviour by virtue of the carbon composite with a probable sign of pseudocapacitor behavior which could be due to the possible functional groups existed on the carbon surface as well as some heteroatom as observed in the EDS analysis. To the same extent, the acidic electrolytes gave a better 6n7CV shape (Figure 3.5A(a-d)) with a larger area in comparison to salt electrolytes (Figure 3.5A(e, f)). The figure suggests a priority of performance in the case of H_2SO_4 , followed by HCl (Figure 3.5A). For a better and more decisive judgment, GCD studies were done for the investigated electrolytes at a 0.5 A/g current density the same condition of CVs measurements at 0.1 M concentration of all electrolytes (Figure 3.5B). Similar to the CV information, the GCD profiles showed the longest discharging time in the case of using H_2SO_4 as an electrolyte (Figure 3.5B(a)), followed by the other acids of HCl, H_3PO_4 , and HClO_4 in their discharging time (Figure 3.5B(b-d)). In comparison, the salt electrolyte of Na_2SO_4 showed a low discharging time, followed by the NaCl electrolyte with the lowest discharging time amongst the other electrolytes (Figure 3.5B (e, f)).

According to Table 3.1, the DLSNC/Steel electrode gave the highest specific capacitance performance with C_{sp} (measured according to equation (1)) of 113 F/g in 0.1 M H_2SO_4 , which led to select H_2SO_4 as a suitable electrolyte for the following experiments. Similarly, the quasi-rectangular CV shapes and quasi-triangular GCD profiles, along with some unusual curvatures, shows the EDLC accompanied by pseudocapacitance behaviour of the DLSNC/Steel electrode.

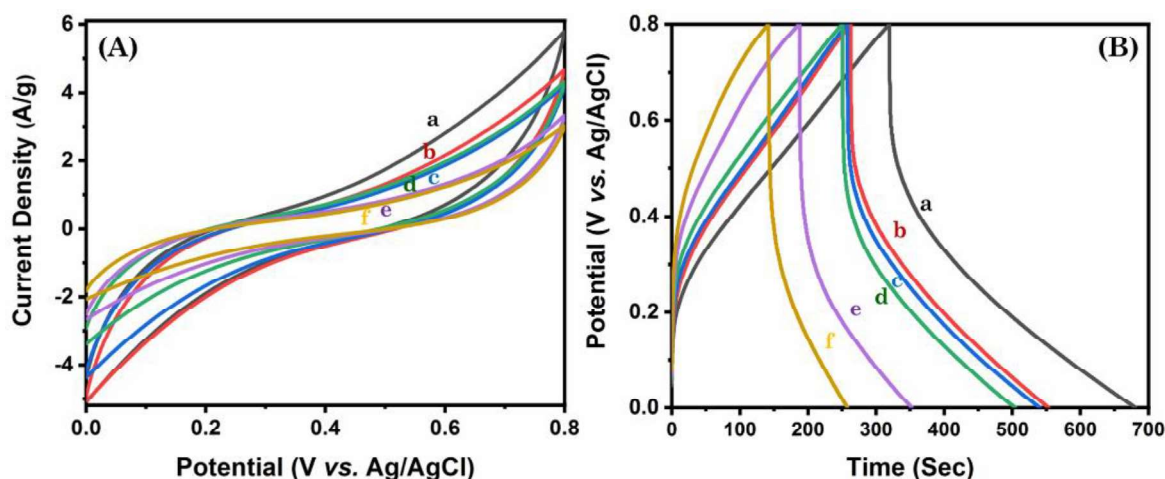


Figure 3.5. (A) CVs of the DLSNC/Steel electrode at a scan rate of 50 mV/sec in 0.1 M of H_2SO_4 (a) HCl (b), H_3PO_4 (c) $HClO_4$ (d), Na_2SO_4 (e), and $NaCl$ (f). (B) GCD profiles recorded in the three-electrode system for the DLSNC/Steel electrode at a 0.5 A/g current density in 0.1 M of H_2SO_4 (a) HCl (b), H_3PO_4 (c) $HClO_4$ (d), Na_2SO_4 (e), and $NaCl$ (f).

Table 3.1. C_{sp} of DLSNC/Steel electrode in different electrolytes recorded in a three-electrode system.

Electrolyte (0.1 M)	C_{sp} (F/g)
H_2SO_4	113

HCl	89
H ₃ PO ₄	87
HClO ₄	78
Na ₂ SO ₄	52
NaCl	36

3.3.3 Electrochemical investigation of DLSNC/Steel toward symmetric supercapacitor by using two electrode system

An electrochemical system of two electrodes was used to record CV, GCD, and EIS of the DLSNC/Steel electrodes-based symmetric supercapacitor. Different scan rates, including 5, 10, 25, and 50 mV/sec, were applied in the CV technique within an operating potential window from 0 to 0.8 V (Figure 3.6A). According to CV measurement, the current density and the area under the CV curves increase with the increase in current density. Also, the quasi-rectangular CV shapes, along with some unusual curvatures, show the EDLC accompanied by pseudocapacitance behavior of the DLSNC/Steel electrode-based symmetric supercapacitor. The C_{sp} were measured at different current densities using equation (2). It was clear that the C_{sp} of the supercapacitor device decreases by increasing the scan rate (Figure 3.6B), which is explained by the high percentage of penetration of ions in the carbon at a low scan rate [42]. It is well known that a slower scan rate provides enough time to entirely diffuse the electrolyte into the electrode materials, whereas a high scan rate provides a shorter time to diffuse the electrolyte into electrode materials [201].

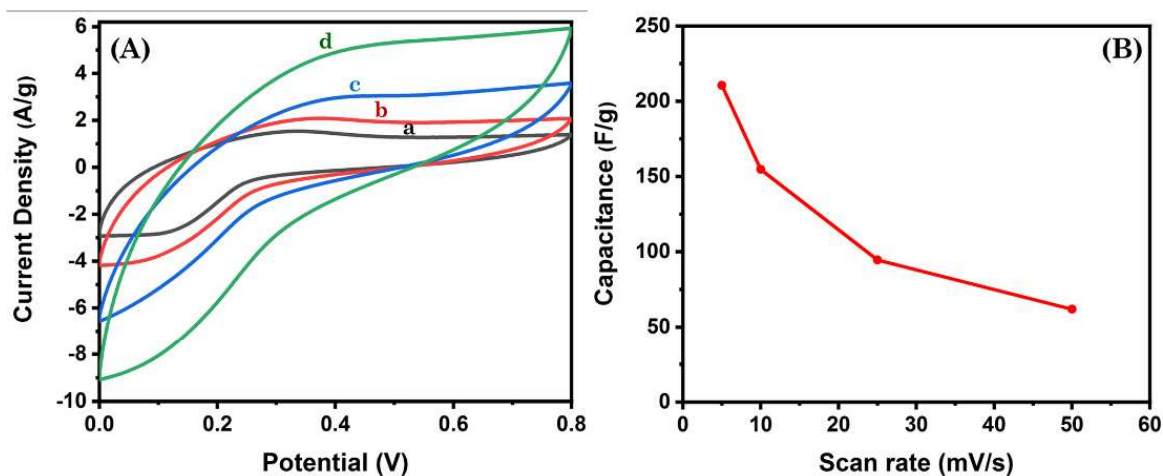


Figure 3.6. (A) CV curves of the DLSNC/Steel based symmetric supercapacitor device in 0.1 M of H₂SO₄ at different scan rates, i.e., 5 (a), 10 (b), 25 (c), and 50 mV/sec (d). (B) Plot of specific capacitance of DLSNC/Steel-based symmetric supercapacitor device vs. scan rates.

To investigate the performance of the DLSNC/Steel based symmetric supercapacitor over a different range of current densities, GCD profiles were recorded over 0.5, 1, 1.5, 2, and 2.5 A/g. The GCD figures revealed a significant decrease of the discharging time with the increase of the current, reflecting a predictable, normal behaviour of the supercapacitor device. Equation (3) was used to measure the C_{sp} of the DLSNC/Steel-based symmetric supercapacitor. The value of C_{sp} of the DLSNC/Steel-based symmetric supercapacitor device is ~ 107 F/g, as it was calculated at a current density of 0.5 A/g within an operating potential window from 0 to 0.8V (Figure 3.7A). Depending on equation (3), the C_{sp} were calculated over the different current densities of 1, 1.5, 2, and 2.5 A/g giving the C_{sp} values of 93, 74, 62, and 50 F/g, respectively. Increasing the current density decreases discharging time, leading to decreased C_{sp} . This could be explained by increasing current density and the distractions towards the electrolyte ions infiltrating the electrode

materials and their pores due to increased current. Consequently, it causes decreasing the electrolyte ions captured on the surface and reduces its C_{sp} [42].

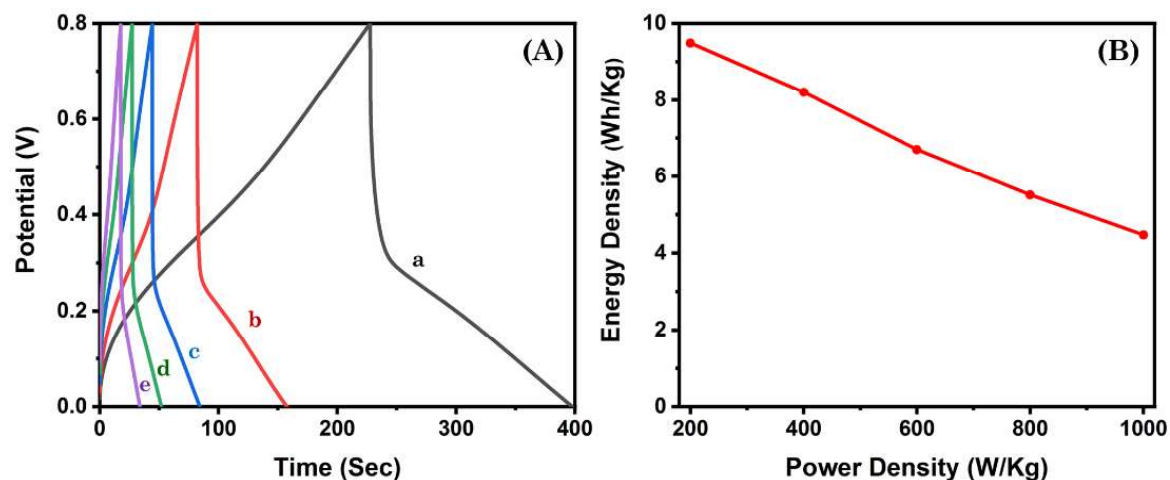


Figure 3.7. (A) GCDs at 0.5 (a), 1 (b), 1.5 (c), 2 (d), and 2.5 A/g for demonstration of the charging/discharging behavior. (B) Ragone plot of DLSNC/Steel based symmetric supercapacitor device.

The densities of energy and power of the DLSNC/Steel based symmetric supercapacitor device were measured from the GCD data using equation (4) and equation (5), respectively. The DLSNC/Steel-based symmetric supercapacitor exhibited a 10 Wh/Kg of energy density for a 200 W/Kg power density. Both values were measured at a current density of 0.5 A/g and applied potential window from 0 to 0.8 V. Different energy and power densities values were calculated at different current densities, and the Ragone plot was plotting as shown in Figure 3.7B. The plot of the DLSNC/Steel-based symmetric supercapacitor shows a standard behavior of the supercapacitor by increasing the power density of the energy density decreases.

To evaluate the cyclic stability of the fabricated DLSNC/Steel-based symmetric supercapacitor, 1000 GCD cycles were recorded at a current density of 3.5 A/g. Figure 3.8A displays the capacitance retention of the supercapacitor remained higher than 92% for the 1000 cycles. The Nyquist plots of the DLSNC/Steel-based symmetric supercapacitor before and after the stability test are shown in Figure 3.8B. The equivalent series resistance (R_{ESR}) of the DLSNC/Steel-based symmetric supercapacitor, which represents the solution resistance, was evaluated from the Nyquist plot by considering the intersection of curves with the X-axis [42]. The charge transfer resistance (R_{CT}) was calculated by measuring the diameter of the semi-circle of the Nyquist plot. To calculate Warburg impedance (W), the slope of the plot of the plot was measured by the equation of its linearity. Where a high slope suggests a better diffusion of ions via the electrode surface and indicates better capacitance performance. Regarding the Nyquist plots, the R_{ESR} was 3.2 Ω before and after the 1000 GCD cycles. Whilst the R_{CT} was lightly changed before and after the stability test from 48.1 to 49.8 Ω , respectively. This slight change is due to the effect of the electrolyte ions trapping in the electrode materials. Furthermore, the W was 0.8 before the stability test and decreased to 0.6 after the 1000 GCD cycles. In general, the change of solution and R_{CT} was slight and could be neglectable. The circuit diagram of the supercapacitor is drawn in the inset of Figure 3.8B.

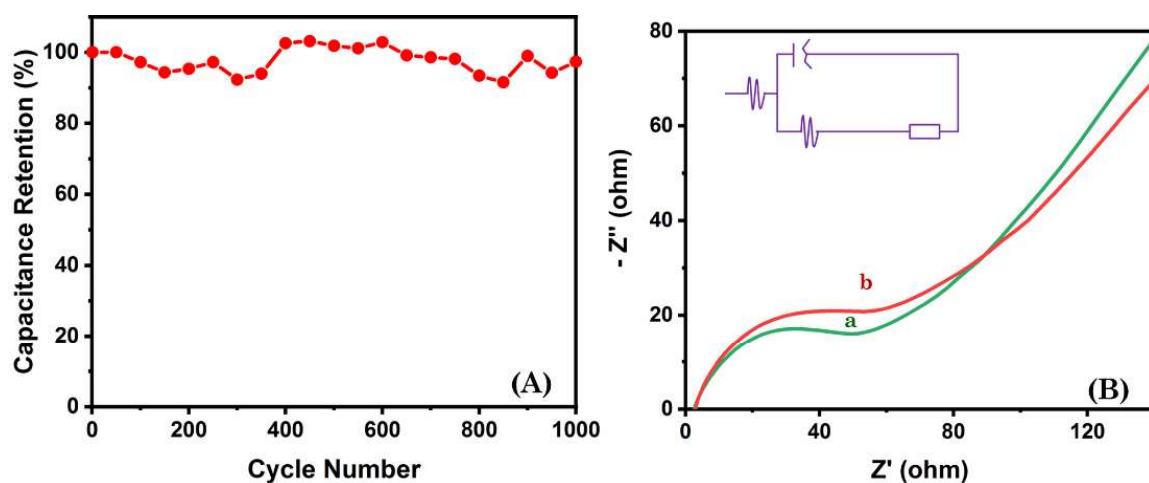


Figure 3.8. (A) Capacitance retention of DLSNC/Steel-based symmetric supercapacitor device at 3.5 A/g current density after 1000 GCD cycles. (B) Nyquist plot (a) before and (b) after stability test of 1000 cycles, the inset shows the equivalent circuit diagram.

Table 3.2. Performance comparison of the date leaves derived submicron/nano carbon-based symmetric supercapacitor device with that of previously reported biomass-derived carbon-based supercapacitors.

Biomass source	Electrolyte	Current density (A/g)	Specific capacitance (F/g)	Energy density (Wh/kg)	Power density (W/kg)	Ref
Oil palm kernel shell	1 M Na ₂ SO ₄	0.5	47	7.4	300	[202]
Chinese fir	1 M H ₂ SO ₄	0.5	111	7.8	500	[203]
Pinecone	1 M H ₂ SO ₄	0.5	43	16.1	464	[204]
Waste coffee grounds	2 M KOH	0.5	105.3	6.94	350	[205]
Graphene	1 M Na ₂ SO ₄	0.2	65	12	400	[206]

foam						
Lima bean	LiCl/PVA gel	0.5	119	4.13	5600	[207]
Rice husk	6 M KOH	0.1	147	5.11	250	[208]
Corn husk	1 M TEABF ₄ / AN	1	127	20	681	[209]
Camellia oleifera	2 M H ₂ SO ₄	0.5	275	9.55	478	[210]
Jute sticks	KOH/Glycerol gel	1	142	20	500	[42]
Date palm leaves	0.1 M H ₂ SO ₄	0.5	107	10	200	This work

3.4 Conclusion

In summary, DLSNC was prepared from biomass, the date Palm leaves, through heat treatment and ball-milling. The characterizations support the sub-nano and nano-meter size carbon particles. Electrochemical investigations of the DLSNC/Steel electrode by CV measurements in a three-electrode system indicate that 0.1 M H₂SO₄ is a suitable electrolyte for the supercapacitor. The final symmetric supercapacitor was fabricated successfully by applying two symmetrical electrodes of DLSNC/Steel separated by a separator saturated by 0.1 M H₂SO₄. In addition, the DLSNC/Steel based supercapacitor was tested for stability over 1000 GCD cycles, maintaining over 92% of specific capacitance. The fabricated symmetric supercapacitor offers an inexpensive tool for storage energy due to the use of common low-cost steel as a substrate and the active material of electrode of DLSNC, which is considered a waste and recycling product of the date palm trees. This study suggests that the DLSNC/Steel based symmetric

supercapacitor could be considered an environmentally friendly and promising energy storage device for mass-production.

CHAPTER 4

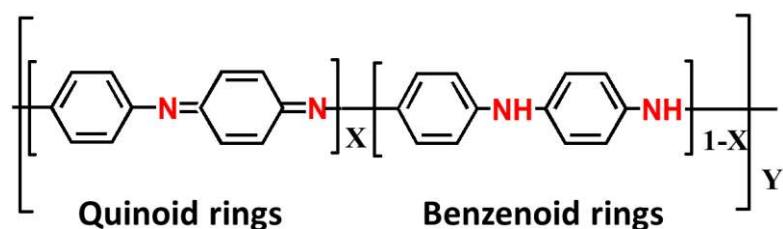
Fabrication of high performance symmetric supercapacitor by using electrodeposition of polyaniline on steel mesh surface

4.1 Introduction

Energy storage has become an essential requirement to meet the increasing needs of our global population of energy demands. Consequently, electrochemical energy storage is becoming an indispensable area in scientific research worldwide [211]. In general, the supercapacitors as an application have high power density, fast charge and discharge, long cycling stability, and a broad range of working temperatures [52, 212-214]. The EDLC has an electrostatic charge-storage mechanism, where the EDLC electrode material attracts the oppositely charged ions of the electrolyte when a voltage is applied [215]. In the case of a pseudocapacitor, the charge-storage mechanism is a faradaic charge transfer [216, 217]. The pseudocapacitor electrode material should contain active redox compounds. This type stores the energy by the chemical reaction in the charge phase and releases the stored energy by opposite reactions in the discharge phase. The hybrid supercapacitor uses electrostatic and electrochemical mechanisms as a charge-storage mechanism [218]. As a result, it shows EDLC and pseudocapacitor behaviors simultaneously. While two types of materials are mostly used in the case of pseudocapacitor fabrication, i.e., metal oxides and metal hydroxides [219] and polymers [220]. Many types of transition metals oxides and hydroxides are reported as electrode

materials of pseudocapacitors, such as cobalt oxide/hydroxide [221], nickel oxide/hydroxide [222]. On the other hand, conductive polymers are used widely to fabricate pseudocapacitor devices due to their tunable electronic conductivity and the high ability to dope different types of active redox materials [223]. Many types of conductive polymer were reported successfully as pseudocapacitor electrode materials, for instance, polyaniline (PANI) [224, 225], polypyrrole [226], thiophene [227], and their derivatives [228]. In this regard, PANI is a frequently used material in different research areas in addition to the supercapacitor field [229]. It started attracting scientists' attention in 1980 due to its properties and easiness of preparation. Since that time, PANI has been used in different research areas, which include drug delivery [230], plastic batteries [231], display devices [232], chemical modified electrodes [233], chemical and biochemical sensors [234], and supercapacitors [235].

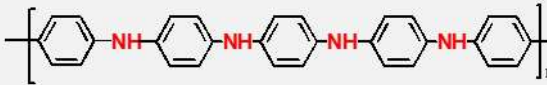
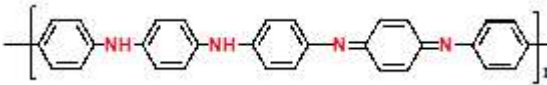
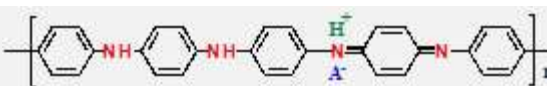
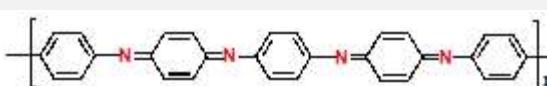
PANI is synthesized from aniline polymerization, which results from the polymer chain formation [236, 237]. In general, the PANI chains have the following formula [238]:



The PANI contains two types of rings which are quinoid and benzenoid. According to the PANI formula, increasing the X value leads to an intensification in the oxidation phase of the polymer, where nitrogen (N) can be completely oxidized in both rings. Whilst

increasing the Y value increases the polymer chain length. It is noteworthy that PANI can be doped with anions which in turn changes PANI into a conductive polymer by increasing the electron orbitals in the polymer chain structures. This type of doped PANI with $X = 0.5$ is called emeraldine salt, which is distinguished for being a conductor from the other types of PANI [237, 239]. With regard, we can differentiate four types of PANI which are leucoemeraldine, emeraldine base, emeraldine salt, and Pernigraniline [240, 241]. Leucoemeraldine PANI contains just quinoid rings, and its N is completely reduced (Table 1) [239, 242-244]. Emeraldine base and salt types are partially oxidized with $X = 0.5$. Emeraldine base is an insulator, while the salt type is the only conductive type as a result of doping with anion. Finally, pernigraniline PANI contains just benzenoid rings with $X = 1$, and its N is fully oxidized [245].

Table 4.1. Types of PANI [263].

Form Name	X	Color	Conductivity	Oxidation status	Formula
Leucoemeraldine (LM)	0	Colorless	Insulator	Completely reduced	
Emeraldine Base (EMB)	0.5	Blue	Insulator	Partially oxidized	
Emeraldine salt (EMS)	0.5	Green	Conductor	Partially oxidized	
Pernigraniline (PE)	1	Purple	Insulator	Completely oxidized	

Specifically, PANI has unique properties (such as a high conductivity [246], a large active surface area due to its nanostructure [239, 247], and a strong ability for doping [239]), which make it an ideal candidate as an electrode material for a supercapacitor [225]. In addition, PANI has a significant pseudocapacitor behavior due to the redox reactions between the oxidized and reduced forms of PANI [248]. Polymerization of PANI can be prepared chemically or electrochemically [249-251]. The electrochemical process of preparation of PANI has many advantages which make it highly desirable. These advantages include being a fast and easy method, using simple instruments, and providing the ability for selective deposition and thickness control [212, 252-255]. Furthermore, the electrochemical method is highly recommended as environmentally friendly due to using a comparatively lower amount of chemical materials and solvents and giving the chance to use alternative sustainable energy [256]. Similarly, selecting the suitable current counter is no less important than the electrode material, when the current counter plays more than one role in the fabrication process [257, 258]. For example, when it is used as an active surface for electro-polymerization in addition to being a current counter in the first place. To fabricate a pseudocapacitor modified with electrodeposited PANI, the current counter should be a suitable catalytic metal in addition to being highly conductive. Many types of electrodes, like gold (Au) [259] and silver (Ag) [260], could be used for electrodeposition of PANI, along with having good conductivity as current collectors. The major disadvantage of the previous electrodes is the significant cost of supercapacitor fabrication. On the other hand, stainless steel material could become a preferable current collector electrode due to its advantages which include high conductivity, wide availability, rust resistance, and low cost [261-

263]. Furthermore, stainless is a popular industrial material that can be prepared in different shapes and sizes. Some available types of stainless steel, like steel mesh, can provide a relatively high surface area to use as a current collector and electro-polymerization substrate.

In this work, we used steel mesh material and PANI to fabricate a high-performing and cost-effective supercapacitor device (Figure 4.1). PANI was deposited on a surface of steel mesh in a solution of aniline in 1 M H_2SO_4 using the cyclic voltammetry (CV) technique (Figure 4.1a). The resulting steel mesh electrode modified with PANI (PANI/SME) was used successfully to fabricate a symmetrical high-performance supercapacitor device (Figure 4.1b, c).

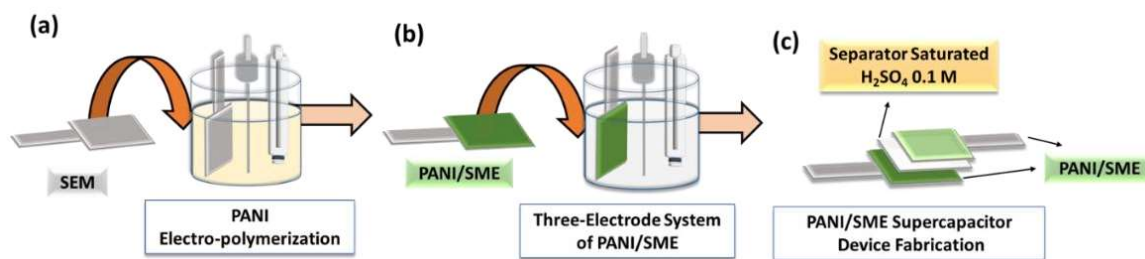


Figure 4.1. The PANI/SME supercapacitor device fabrication process: (a) Electro-polymerization of PANI on the SME as working electrode in a solution of 0.5 M aniline in 1 M H_2SO_4 by using CV technique, Ag/AgCl as reference electrode, and Pt wire as a counter electrode in potential range from 0 to 1 V, at a scan rate of 50 mV s^{-1} , (b) Testing the electrochemical performance of PANI/SME electrode in the three-electrode system using Ag/AgCl as a reference electrode and a Pt wire as a counter electrode in a solution of 0.1 M H_2SO_4 . (c) Fabrication of symmetric supercapacitor device by using two electrodes of PANI/SME separated by a filter paper saturated by 0.1 M H_2SO_4 .

4.2 Experimental

4.2.1 Materials

Aniline was obtained from BDH Chemicals Ltd. Poole England. Hydrochloric acid (HCl) and H_2SO_4 were obtained from MACRON., perchloric acid (HClO_4), ethanol, acetic acid (CH_3COOH), and nitric acid (HNO_3) were procured from Sigma-Aldrich. Phosphoric acid (H_3PO_4) was obtained from Fluka. Good quality steel mesh was purchased from a local company. All the equipment and glasses were cleaned and rinsed with distilled water, and the chemical solutions were prepared using deionized water (DIW).

4.2.2 SME preparation

SMEs were cut by a scissor in a particular dimension to provide a suitably shaped strip. The SME strips were sonicated in ethanol for 15 min. Then, it was rinsed in DIW and cleaned again by sonication in DIW for 15 min. Finally, the SME strips were rinsed in DIW for the second time and dried at a temperature of 50 °C for 30 min in an electric oven.

4.2.3 PANI modified SME preparation

The PANI electrodeposition was accomplished in a solution of 0.5 M of aniline in 1 M H_2SO_4 using the CV technique at 50 mV s^{-1} . The electrodeposition was done using a potential window (PW) from 0 to 1 V for 15 cycles in a three-electrode system. The SME, Ag/AgCl, and Pt wire were used as a working electrode (WE), reference electrode (RE), and counter electrode (CE), respectively. After applying CV measurements, the green layers of PANI started forming on the SME. The polymerization process was

stopped after optimized 15 cycles, and the formed PANI/SME was rinsed gently with DIW and kept drying at room temperature.

4.2.4 Fabrication of PANI/SME based symmetric supercapacitor

Two of the prepared PANI/SME (geometrical area 1 cm²) were used as two electrodes separated with a separator (filter paper) saturated with a solution of H₂SO₄ (0.1 M) to fabricate the PANI/SME based symmetric supercapacitor.

4.2.5 Electrochemical measurements

Different electrochemical measurements were done to calculate the performance of the developed supercapacitor, including CV, galvanostatic charge/discharge (GCD), and electrochemical impedance spectroscopy (EIS). The electrochemical parameters of the experiments were performed with an electrochemical workstation (760E-CHI, CH Instruments, Inc., USA). Basic electrochemical properties of the WE materials (PANI/SME) were also tested using a three-electrode electrochemical system. Here, Ag/AgCl and platinum wire were used as RE and CE, respectively. The areal capacitance of the tested electrodes by using the three electrode system was calculated based on Eq. (6), the areal capacitance (C_{ar}) of the supercapacitor using the two electrode system was calculated based on Eq. (7) [42, 44, 79, 191].

$$C_{ar} = \frac{\int I dV}{2 \times S \times v \times \Delta V} \quad (6)$$

$$C_{ar} = \frac{\int I dV}{S \times v \times \Delta V} \quad (7)$$

The C_{ar} represents the areal capacitance measured by the unit of Farad cm⁻² (F cm⁻²), $\int I dV$ signifies the integrated area value under the CV measured by the unit of watt (W),

S denotes the area of the active electrode material measured by the unit of (cm⁻²), v is the scan rate measured by the unit of V s⁻¹, and ΔV represents discharging potential voltage range measured by the unit of a volt (V).

The C_{ar} of the tested electrodes was calculated based on Eq. (8) from the GCD figures [42, 52, 212, 225].

$$C_{ar} = \frac{I \times t}{S \times \Delta V} \quad (8)$$

The C_{ar} represents the areal capacitance measured by the unit of F cm⁻², I represent the discharging current used by the unit of Ampere (A), t symbolizes the discharging time measured by the unit of second (s), S represents the mass of the active electrode material measured by the unit of (cm²), and ΔV represents discharging potential voltage range measured by the unit of volt (V).

According to the supercapacitor device performance, other essential values are energy density (E), which was calculated depending on Eq. (9), and power density (P), which was calculated depending on Eq. (10) [43, 264].

$$E = \frac{1}{2} \times \frac{C_{ar} \Delta V^2}{3600} \quad (9)$$

$$P = \frac{3600 \times E}{\Delta t} \quad (10)$$

E is the energy density measured by the unit of W h cm⁻², C_{ar} represents the areal capacitance measured by the unit of F cm⁻², ΔV represents the applied potential range measured by the unit of volt (V), P is the power density calculated by the unit of W cm⁻², and Δt signifies the discharging time measured by the unit of s.

4.3 Results and discussions

4.3.1 Electrodeposition of PANI on SME and electrochemical characterization of PANI/SME electrode

PANI was deposited on SME at 50 mV s^{-1} in a solution of 0.5 M aniline in 1 M sulfuric acid in an OPW from 0 to 1 V using Ag/AgCl as a RE and platinum wire as a CE. **Figure 1A** indicates the CV curves of 15 cycles for the electro-polymerization of PANI on the SME. The current density of the voltammogram rises by increasing the polymerization cycle number, indicating the PANI growth on the SME surface. In the initial positive potential sweep cycles, the mono-aniline oxidized around 0.85 V (vs. Ag/AgCl), showing a distinct irreversible oxidation peak. By the PANI deposition, the height of the aniline oxidation peak decreases and disappears later throughout the deposition process. Two anodic peaks are noticeable at 0.3 V and 0.6 V, which are attributed to the oxidation of LM to EMS and EMS to PE, respectively. While the reduction peaks around 0.1 V and 0.4 V are attributed to the reversible reactions.[237, 238, 265] The oxidation and reduction peaks shift by increasing the cycle number due to the growth of the PANI on the SME surface, which increases the current density and shifts the redox potential.

CV curves of the three PANI/SMEs and a bare SME were recorded using a three-electrode system to calculate the effect of the number of polymerization cycles on the capacitance performance (Figure 4.2B, C). The CV measurement was accomplished at 50 mV s^{-1} in a solution of 0.1 M sulfuric acid using Ag/AgCl and platinum wire in an OPW from -0.4 V to 0.8 V. The three PANI/SMEs were designed with different deposition cycle numbers of 5, 10, and 15 cycles. The area under CV curves increased with a greater

number of cycles, which indicates to increase in the capacitance of PANI/SME. However, the film prepared using > 15 deposition cycles was not stable. As a result, the deposition of PANI was limited to 15 cycles. The PANI/SMEs prepared by deposition cycle numbers of 10 and 15 cycles show one oxidation peak around 0.5 due to the oxidation of LE into EMS (Figure 4.2B (a, b)). The oxidation peak shifts toward more positive potential in the case of the electrode surface prepared by the high deposition cycle number due to the increase of the PANI surface and the current density. For the same two PANI/SME surfaces, two cathodic peaks are noticeable around -0.1 and 0.5 V attributed to the reduction of EMS into LE and PE into EMS, respectively. Similarly, the two oxidation peaks shift into the more negative potential in the PANI/SME surface prepared by the high deposition cycle number. The PANI/SME prepared by deposition cycle numbers of 5 cycles shows three oxidation peaks (0.1, 0.5, and 0.7 V) (Figure 4.2C). The two oxidation peaks around 0.1 and 0.7 V attributed to LE oxidation into EMS and PE, respectively. While the oxidation peak around 0.5 is attributed to dimers oxidation.[237, 238, 265] This peak disappears with the growth of the PANI. All the PANI/SMEs show much higher capacitance than the bare SME. The bare SME shows a small CV area with a current density in the rank of μA (Figure 4.2C, D). Furthermore, the bare SME voltammogram shows two oxidation peaks around -1 and 0.4 V and two reduction peaks around 0.05 and 0.6 V attributed to the redox of stainless-steel metals of Fe and Ni (Figure 4.2D). However, the PANI/SME prepared by deposition cycle number of 15 cycles was selected as an optimized electrode due to its high capacitance compared to the other PANI/SMEs. In addition, PANI/SME with a higher deposition cycle number (more than 15) shows unstable dense PANI layers.

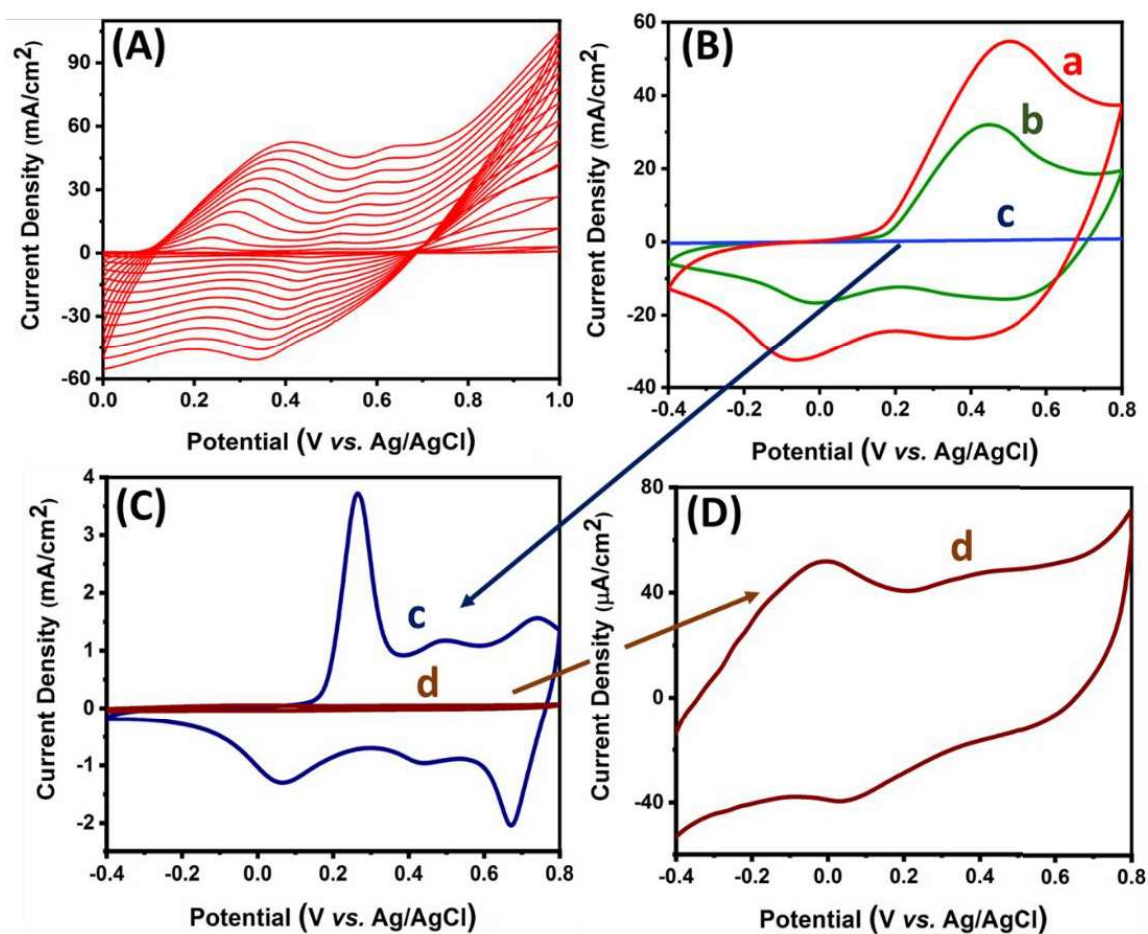


Figure 4.2. (A) CV curves of 15 cycles for electro-polymerization of PANI on the SME at 50 mV s⁻¹ in a solution of 0.5 M aniline in 1 M sulfuric acid, (B) CV curves of PANI/SME electrode prepared by polyaniline deposition at different CV cycles, i.e., 15 (a), 10 (b), and 5 cycles (c) in 0.1 M sulfuric acid measured at 50 mV s⁻¹, (C) CV curves of PANI/SME electrode prepared by polyaniline deposition CV cycle numbers of 5 cycles (c), and bare SME (b) in 0.1 M sulfuric acid measured at 50 mV s⁻¹, (D) CV curves of a bare SME in 0.1 M sulfuric acid measured at 50 mV s⁻¹.

4.3.2 Structural and morphological characterization

The synthesized PANI on SME was investigated using the XRD (Figure 4.3A). The XRD pattern shows the PANI structure in the sample. The broad peaks between $2\theta = 10^\circ$ and $2\theta = 30^\circ$ confirm that the formed PANI contains an amorphous structure. The crystal peaks at $2\theta = 9.9^\circ$, 21.1° , 24.8° , 25.9° and 27.1° indicate (001), (020), (200), (110), and (111) crystal planes, respectively, which indicates the emeraldine salt form of PANI [266-271]. While the peaks at $2\theta = 21.1$ and 19.5 are associated with the frequency of parallelity and perpendicularity to the PANI chain [272]. Similarly, the FTIR confirms the structure of PANI (Figure 4.3B). The peak at 582 cm^{-1} indicates the presence of C-N-C bonding mode in the aromatic ring. While the peak at 713 cm^{-1} indicates carbon-carbon and carbon-hydrogen bonds in the benzene ring [268, 270]. A peak at 825 cm^{-1} indicates the presence of C-H out-of-plane bonding in the benzenoid ring. The peak at 1120 cm^{-1} shows the presence of S=O bonding due to the SO_4^{2-} ions doping [268, 270]. The peaks at 1233 , 1296 , and 1488 cm^{-1} indicate the presence of C-N stretching in the benzenoid ring. The peak at 1563 cm^{-1} indicates the presence of C=N stretching in the quinoid ring [268, 270]. The peak at 2930 cm^{-1} manifests the symmetric stretch vibration band of methylene $[-(\text{CH}_2)_n-]$ [268, 270]. Finally, the peak at 3403 cm^{-1} indicates -OH due to moisture. As a result, The FTIR spectrum exhibits different chemical bonds which belong to both types of benzenoid and quinoid rings. Furthermore, the spectrum confirms the emeraldine form of PANI forming [268, 270]. In addition, S=O bonding which belongs to the presence of SO_4^{2-} ions, confirms the emeraldine salt-forming [268, 270, 273, 274].

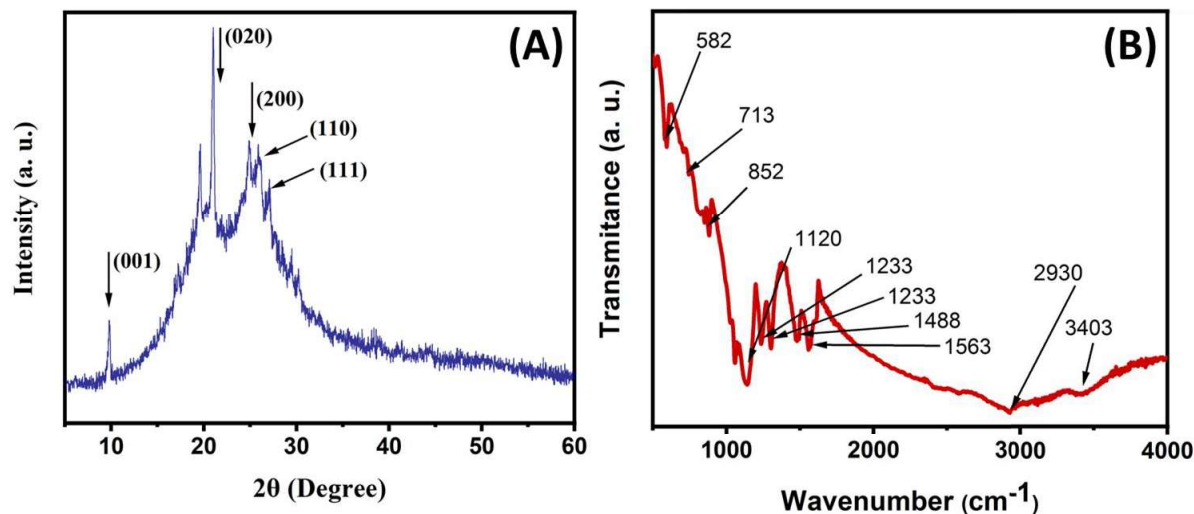


Figure 4.3. (A) XRD pattern and (B) FTIR spectrum of the synthesized PANI on SME in a solution of mono-aniline (0.5 M) in H₂SO₄ (1 M) by using the CV technique at 50 mV s⁻¹ in a potential window from 0 to 1 V (vs. Ag/AgCl) for 15 cycles in a three-electrodes system.

The morphological study of SME and PANI/SME surfaces was investigated by FESEM images at different magnifications (Figure 4.4). The bare SME images show a metallic net with criss-cross stainless steel wires and regular apertures (Figure 4.4(a, c)). The SME wire width is around 75 μm, while the net apertures have a square shape with a square side of approximately 100 μm (Figure 4.4b). According to the highly magnified images, the SME has a metallic plan surface with scarce small bumps (Figure 4.4(e, g, and i)). On the other hand, the PANI/SME FESEM images display a compact porous layer of polymer covering the SME's metallic net. Clearly, the polymer layer formed around the stainless steel wires, leaving slot-like openings (Figure 4.4(f, g)). The length of the opening ranges between 75 to 150 μm, while the width ranges from 40 to 20 μm (Figure 4.4g). The high magnified images show a rich porous surface with a coral morphology

(Figure 4.4(h, i, and j)). PANI grew on the SME surface, creating a cross-sectional fibril network with pores dimension around approximately $2\text{ }\mu\text{m}$ (Figure 4.4(h, j)).

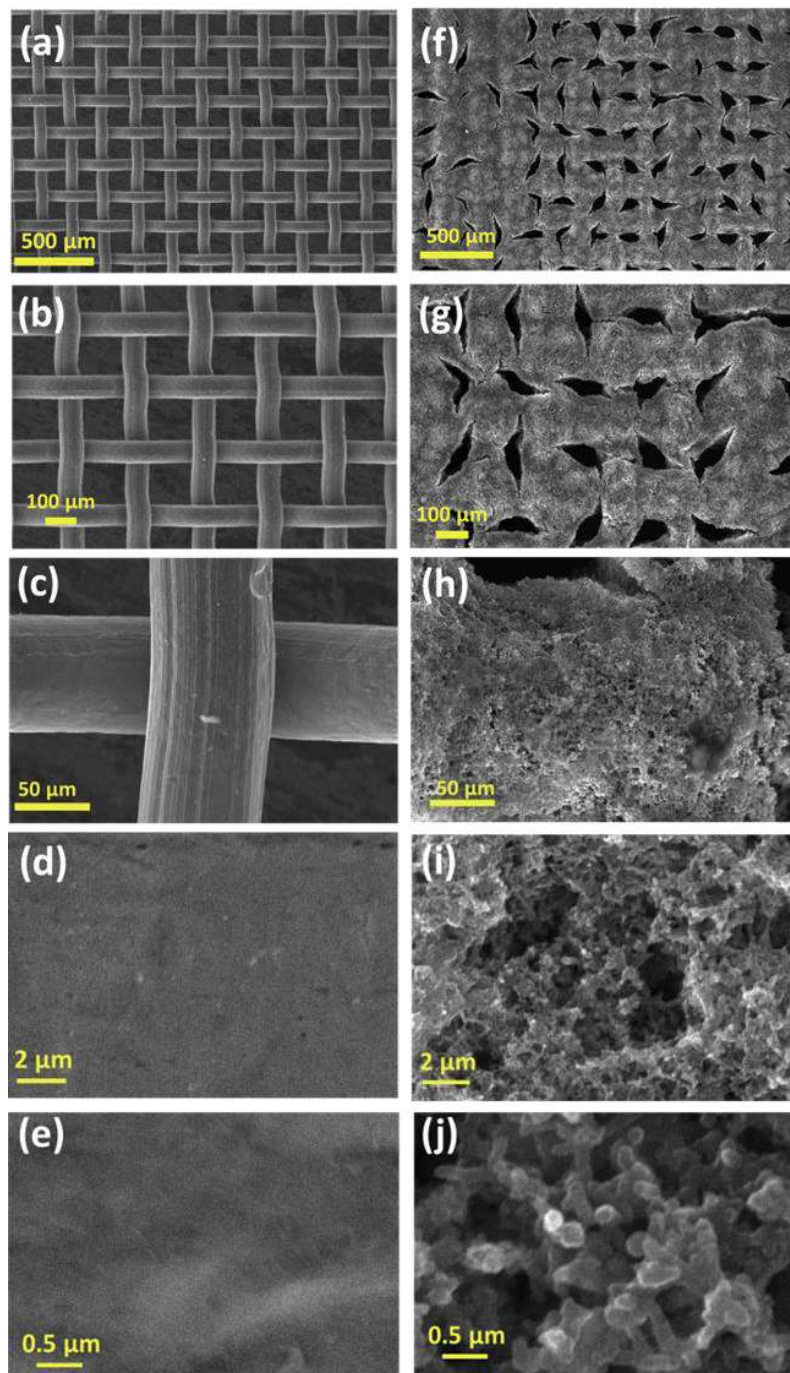


Figure 4.4. FESEM images of (a-e) SME and (f-j) PANI/SME.

The chemical composition of the SME and PANI/SME was investigated by EDS and the elemental mapping of the existing elements (Figure 4.5). The EDS spectrum of SME shows the existence of iron (Fe), chromium (Cr), nickel (Ni), and carbon (C) (Figure 4.5). Elemental mapping images display a high-density distribution of Fe as it is the main component in stainless steel material (Figure 4.5b). Like that, the elemental mapping images show a high-density distribution of Cr as it is used in a high percentage in the stainless steel alloy to increase the alloy's corrosion resistance (Figure 4.5c). However, the elemental mapping images show a lower density distribution of Ni and C (Figure 4.5d, e).

The EDS spectrum of PANI/SME shows the existence of carbon (C), nitrogen (N), sulphur (S), oxygen (O), iron (Fe), chromium (Cr), and nickel (Ni) (Figure 4.6). The existence of C and N is explained due to the PANI covering the SME (Fig. 4b, c). While the existence of S and O is attributed to the sulphate doping in PANI (Figure 4.6d, e). Furthermore, the spectra and elemental mapping images show the existence of Fe, Cr, Ni, and part of C belonging to the stainless steel alloy, as shown previously (Figure 4.6f-h).

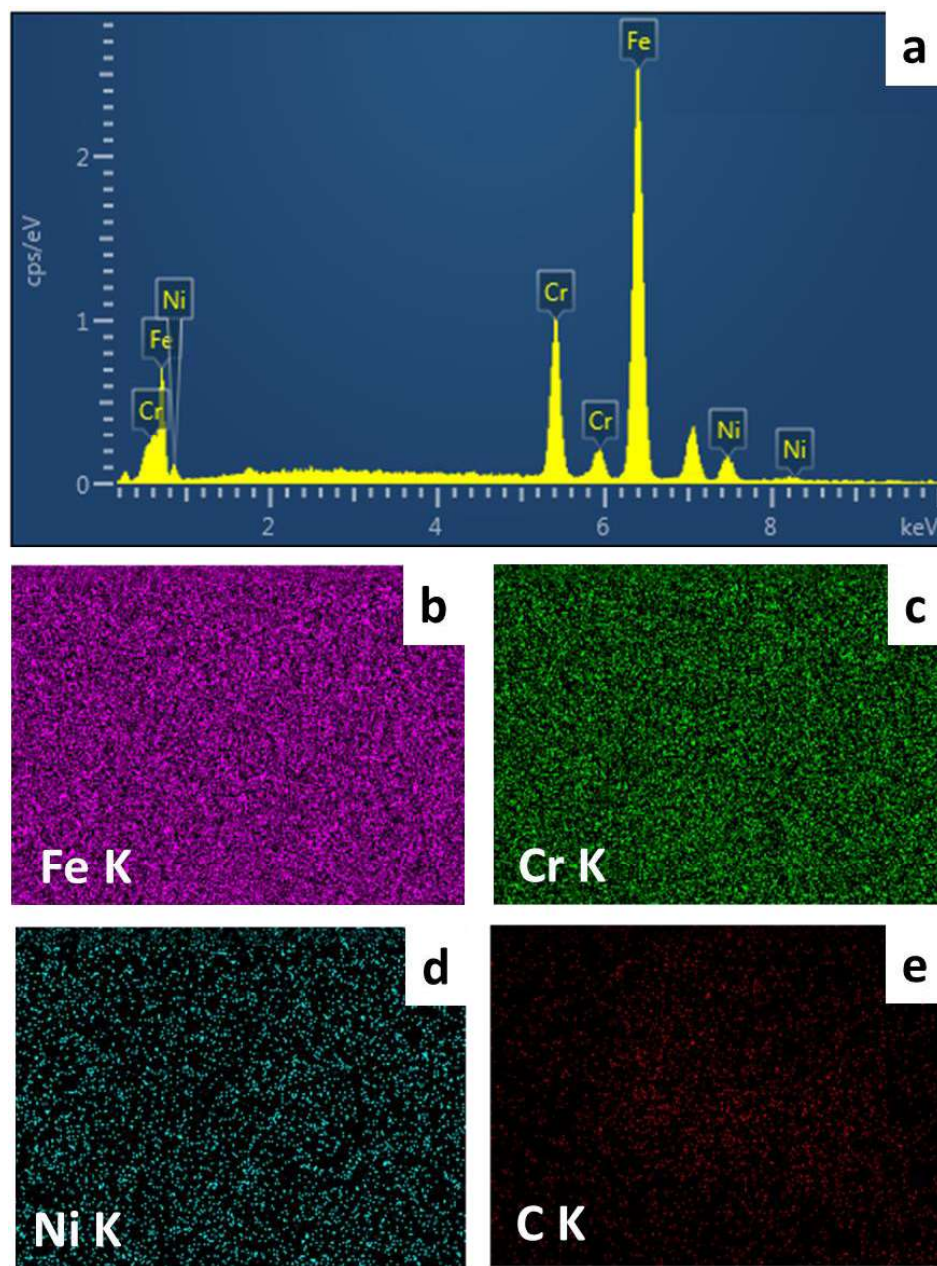


Figure 4.5. EDS spectrum and elemental mapping of the SME, EDS spectrum (a), Fe (b), Cr (c), Ni (d), C (e).

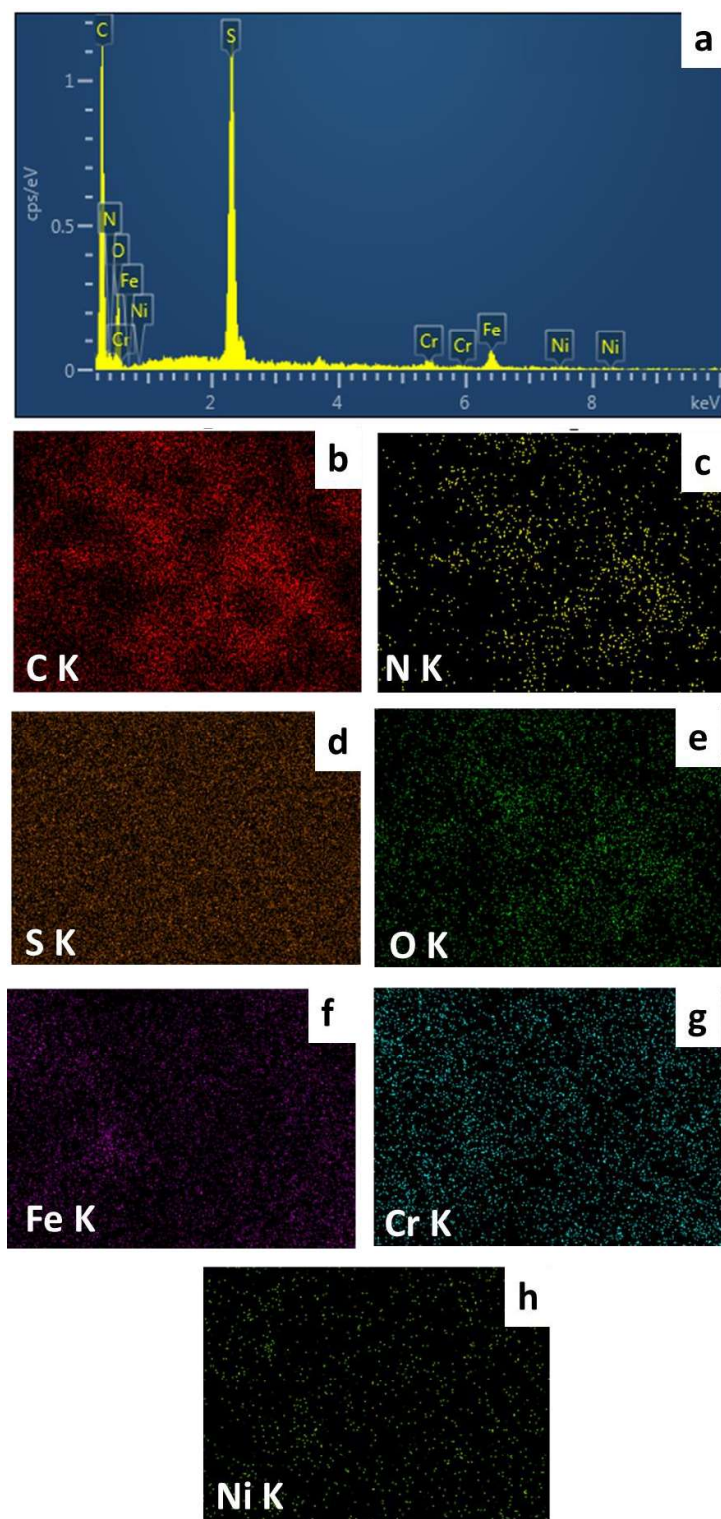


Figure 4.6. EDS spectrum and elemental mapping of the PANI/SME EDS spectrum (a), C (b), N (c), S (d), O (e), Fe (f), Cr (g), and Ni (h).

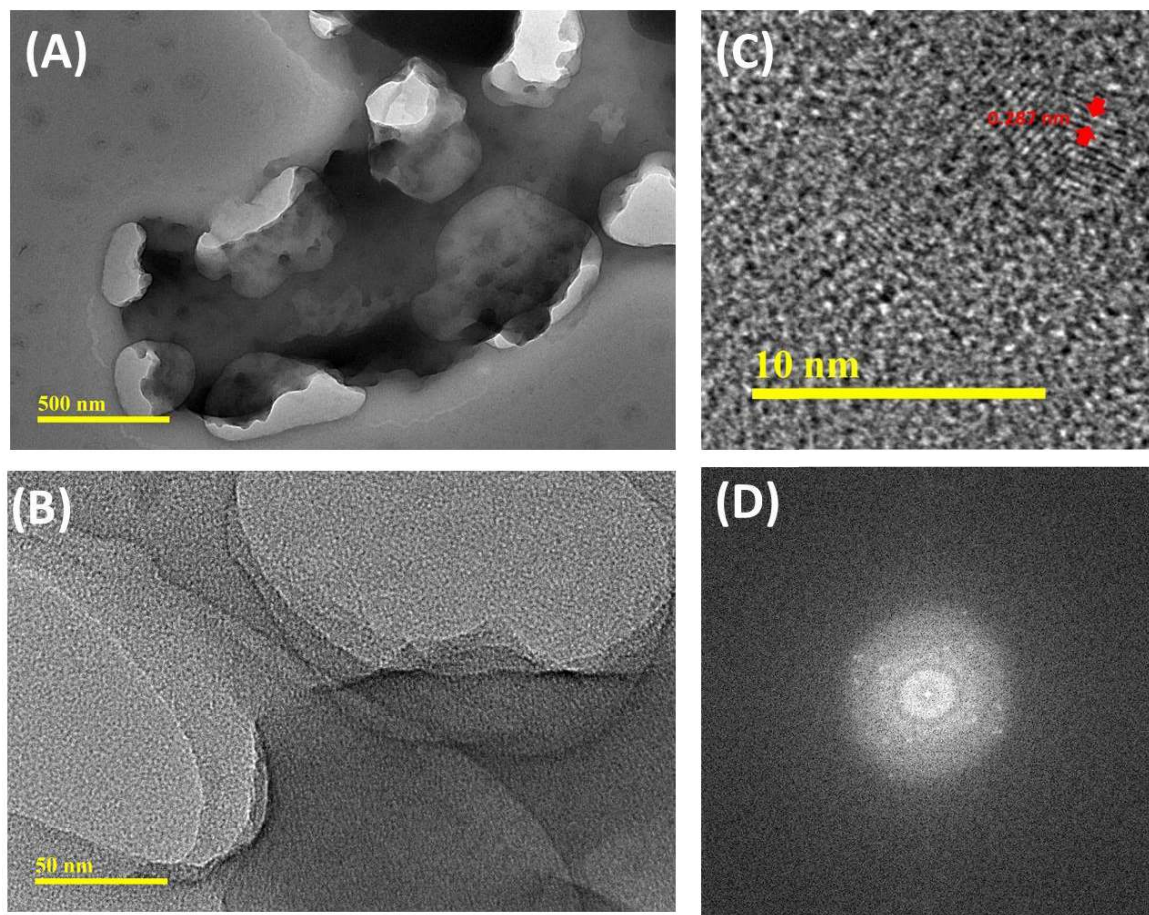


Figure 4.7. TEM images of the synthesized PANI on SME in a solution of mono- aniline (0.5 M) in H_2SO_4 (1 M) by using the CV technique at 50 mVs^{-1} in a potential window from 0 to 1 V (vs. Ag/AgCl) for 15 cycles in a three-electrodes system.

Figure 4.7 shows the TEM images of the synthesized PANI on SME. (Figure 4.7A) illustrates the porous nature of PANI. The sheet type layer structure is observed in the high resolution images of (Figure 4.7B). In addition, the TEM images confirm the existence of both structures of amorphous and crystalline PANI (Figure 4.7C). The lattice spacing was determined in the lattice structure area observed in (Figure 4.7C) to be 0.287 nm associated with (020) crystal plane [271]. Furthermore, selected area

electron diffraction (SAED) pattern confirmed the existence of crystal structure in the synthesized PANI on the steel (Figure 4.7D).

4.3.3 Electrochemical study of the fabricated supercapacitor

To scrutinize the electrochemical behavior of the PANI/SME electrodes in a symmetric supercapacitor, CV, GCD, and EIS measurements were recorded using the two-electrode system in different two PWs of 0 – 0.4 V and 0 – 0.8 V (Figure 4.8) and (Figure 4.9). The two PWs were selected to investigate the fabricated SC performance and mechanism in the different selected PWs. Firstly, the symmetric supercapacitor with PANI/SME electrodes was tested by CV at different scan rates, i.e., 10, 25, 50, 75, and 100 mV sec⁻¹ within an applied PW from 0 to 0.4 V (Figure 4.8B). It is noticeable that the current density and the area under the CV curves increase due to the rise in scan rate. The CV curve has a quasi-rectangular shape in addition to some unusual curvatures. The shape of the figure indicates a dominant double layer mechanism along with a limited pseudocapacitance behavior. The C_{ar} was calculated for the CV curves using the Eq. (2). According to (Figure 4.8B), The C_{ar} increases as the scan rate value decreases. The lower scan rate provides more time to increase the number of electrolyte ions that diffuse the electrode materials [42, 201, 275]. Conversely, a high scan rate value provides a shorter time for the diffusion of electrolyte ions into electrode materials.

The PANI/SME SC was tested. The GCD profiles were measured over 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, and 5 mA cm⁻² using the PW from 0 to 0.4V (Figure 4.8C). The discharging time of the supercapacitor reduces with the rise of the current density, which shows a typical supercapacitor behavior. The equilateral triangle shape of the GCD profiles reflects the dominant double-layer behavior. In addition, the slight pseudocapacitance

behavior appears clearly according to the GCD profile shape. The C_{ar} of the supercapacitor in the potential window from 0 to 0.4 V was calculated using Eq. (3). At a current density of 1 mA cm^{-2} , the C_{ar} is $\sim 353 \text{ mF cm}^{-2}$. The value of the C_{ar} drops with the surge in the current density. The C_{ar} was calculated over the rest of the current densities' values of 1.5, 2, 2.5, 3, 3.5, 4, 4.5, and 5 mA cm^{-2} giving the C_{ar} values of 315, 300, 276, 264, 254, 240, 217, and 210 mF cm^{-2} , respectively. The decrease in the C_{ar} value could be explained by the distractions towards the electrolyte ions infiltrating into the electrode materials and their pores due to increased current [42].

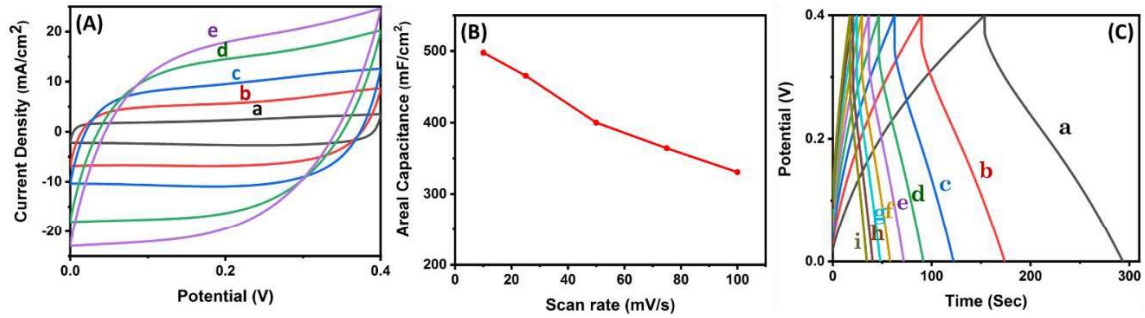


Figure 4.8. (A) CVs of PANI/SME based symmetric supercapacitor device measured at potential window from 0 to 0.4 V at different scan rates of 10 (a), 25 (b), 50 (c), 75 (d), and 100 mV s^{-1} (e), (B) areal capacitance of PANI/SME based symmetric supercapacitor device measured at different scan rates at same PW from 0 to 0.4 V, (C) GCDs of PANI/SME based symmetric supercapacitor device measured from 0 to 0.4 V at different current density of 1 (a), 1.5 (b), 2 (c), 2.5 (d), 3 (e), 3.5 (f), 4 (g), 4.5 (h), and 5 mA cm^{-2} (i) for demonstration of the charging and discharging behavior.

The PANI/SME electrodes-based symmetric supercapacitor performance was investigated using the potential window from 0 to 0.8 V (Figure 4.9A). Different scan rates of 10, 25, 50, 75, and 100 mV s^{-1} were tested (Figure 4.9A). The C_{ar} increases by

decreasing the scan rate, which reflects a standard supercapacitor behavior (Figure 4.9B). According to the cyclic voltammogram shape, the supercapacitor shows a pseudocapacitance behavior due to the redox reaction of the PANI. The figures display an oxidation peak around 0.3 V, and a reversible reduction peak around 0.1 V. The oxidation peak is attributed to the oxidation of LM into EMB. In contrast, the reduction peak is due to EMB's reduction into LM. GCDs measurements were done over different current densities of 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, and 5 mA cm⁻² using the PW from 0 to 0.8V (Figure 4.9C). Using Eq. (3), the C_{ar} is ~ 297 mF cm⁻². While The C_{ar} of the supercapacitor for the current densities of 1.5, 2, 2.5, 3, 3.5, 4, 4.5, and 5 mA cm⁻² were 279, 267, 256, 255, 241, 235, 225, and 213 mF cm⁻², respectively.

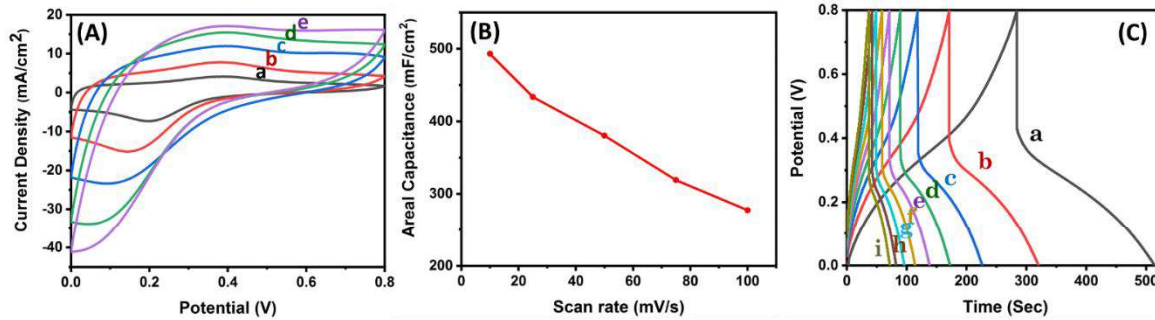


Figure 4.9. (A) CVs of PANI/SME based symmetric supercapacitor device measured at potential window of (0 to 0.8 V) at different scan rates of 10 (a), 25 (b), 50 (c), 75 (d), and 100 mV s⁻¹ (e), (B) the areal capacitance of PANI/SME based symmetric supercapacitor device measured at different scan rates using the potential window from 0 to 0.8 V, (C) GCDs of PANI/SME based symmetric supercapacitor device measured at from 0 to 0.8 V at different densities of 1 (a), 1.5 (b), 2 (c), 2.5 (d), 3 (e), 3.5 (f), 4 (g), 4.5 (h), and 5 mA cm⁻² (i) for demonstration of the charging/discharging behavior.

The cyclic stability test of the PANI/SME electrodes-based symmetric supercapacitor was measured for 1000 GCD cycles. For the PW from 0 to 0.4 V, the stability test was recorded at a current density of 15 mA cm^{-2} (Figure 4.10A). The (Figure 4.10A) does not illustrate any significant decrease in the value of the C_{ar} of the supercapacitor after the 1000 GCD cycles. While the stability test was recorded at 10 mA cm^{-2} for from 0 to 0.8 V. (Figure 4.10B). Similarly, the figure does not show any significant decrease in the value of C_{ar} of the supercapacitor after the 1000 GCD cycles.

The energy density (E) and power density (P) of the PANI/SME electrodes symmetric supercapacitor were measured from the GCD data using Eq. 4 to calculate the E and Eq. 5 to calculate the P. The supercapacitor's E and P were calculated at different current densities of 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, and 5 mA cm^{-2} using both potential windows of 0 to 0.4 V and 0 to 0.8 V. At 1 mA cm^{-2} , the PANI/SME electrodes-based symmetric supercapacitor revealed an energy density ($\sim 7.8 \text{ } \mu\text{W h cm}^{-2}$) for a power density ($\sim 199 \text{ } \mu\text{W cm}^{-2}$). At the same current density for the potential range 0 - 0.8 V, the PANI/SME electrodes-based symmetric supercapacitor exhibited an energy density ($\sim 26.4 \text{ } \mu\text{W h cm}^{-2}$) at a power density ($\sim 400 \text{ } \mu\text{W cm}^{-2}$). The resulting energy and power densities were used to design the Ragone plot (C). The plot of the PANI/SME supercapacitor displays a standard behavior of the supercapacitor by increasing the power density of the device, the energy density decreases. It is noticeable that the energy density values of the supercapacitor measured by using the PW from 0 to 0.8 V are much higher than the E values in the case of using the PW of (0 - 0.4 V) in all the current density values used in the measurement. In addition, the power density values for the PW from 0 to 0.8 V are higher than those for the potential window from 0 to 0.4 V. As a result, the PANI/SME

electrodes-based symmetric supercapacitor showed a higher capacitance relatively in the case of using the range of 0 - 0.4 V. On the contrary, it exhibited a higher power density and energy densities using PW from 0 to 0.8 V (Table 4.2).

Table 4.2. Performance comparison of the PANI/SME based symmetric supercapacitor using different potential windows of 0 to 0.4 V and 0 to 0.8 V.

Potential window (V)	Current density (mA cm ⁻²)	Areal capacitance (mF cm ⁻²)	Energy density (μW h cm ⁻²)	Power density (μW cm ⁻²)
0 – 0.4	1	~ 353	~7.8	~199
0 – 0.8	1	~ 297	~26.4	~400

The Nyquist plots of the PANI/SME electrodes-based symmetric supercapacitor before and after the stability test by applying the PW of 0 to 0.8 V are shown in (Figure 4.10D). The solution resistance, which is the equivalent series resistance (R_{ESR}) of the PANI/SME electrodes-based symmetric supercapacitor was calculated from the Nyquist plot by measure the intersection of curves with the X-axis [201, 212]. Regarding the Nyquist plots, the R_{ESR} was 2.6 Ω before and 1.9 after the 1000 GCD cycles. At the same time, the R_{ct} was lightly changed before and after the stability test from 0.33 to 0.41 Ω , respectively (Figure 4.10D). This slight change is due to the effect of the electrolyte ions trapping in the electrode materials. Furthermore, the W was 7.6 before the stability test and 10.5 after the 1000 GCD cycles. As a result, the change in R_{ESR} and R_{CT} was slight

and could be neglectable. In addition, the increase of the W value indicates the high stability of the supercapacitor even for a higher number of cycles. To evaluate the performance of the PANI/SME electrodes-based symmetric supercapacitor with the previous PANI based works in literature, the supercapacitor shows a competitive performance, as shown in (Table 4.3).

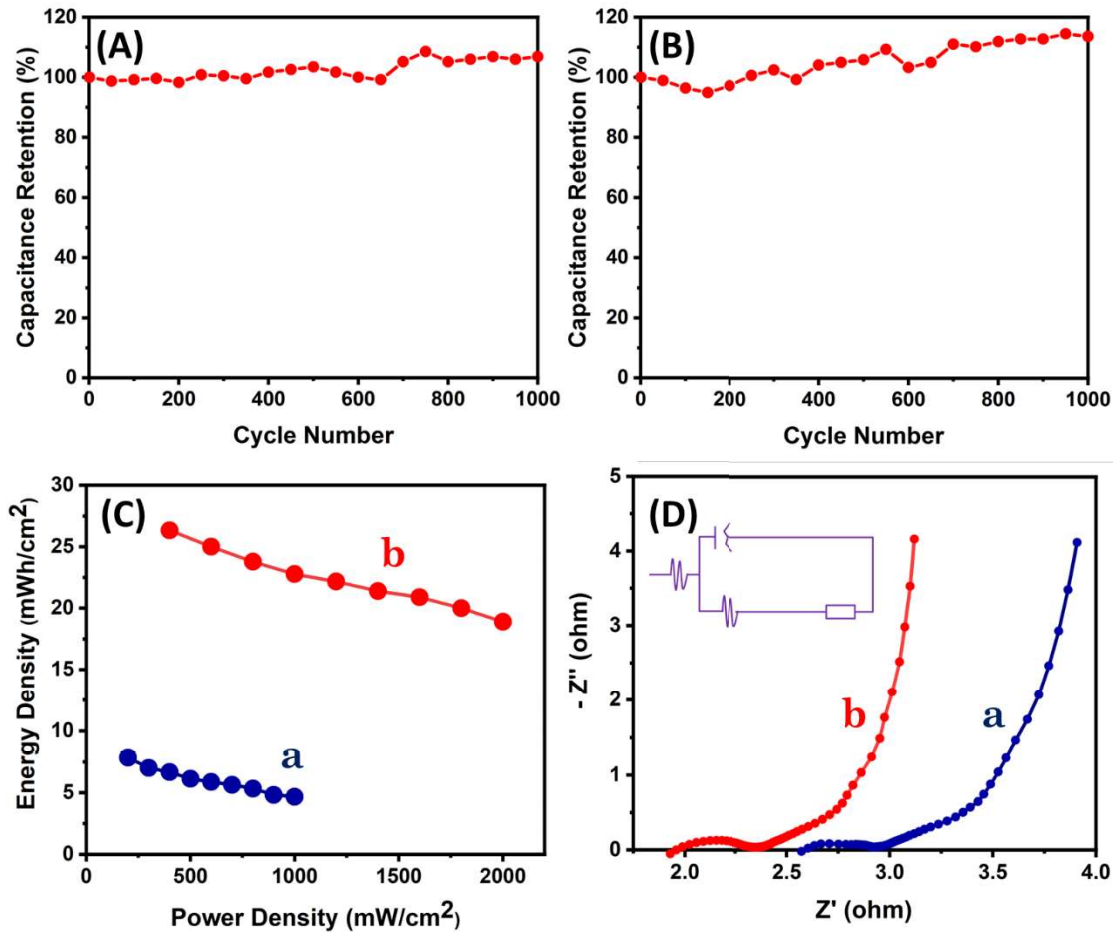


Figure 4.10. (A) Capacitance retention of PANI/SME based symmetric supercapacitor device measured from 0 - 0.4 V at a current density of 15 mA cm⁻² after 1000 GCD cycles, (B) Capacitance retention of PANI/SME based symmetric supercapacitor device measured from 0 - 0.8 V at the current density of 20 mA cm⁻² after 1000 GCD cycles, (C) Ragone plot of the PANI/SME based symmetric supercapacitor device measured at

different current densities at different potential ranges from 0 to 0.4 (a), and 0 to 0.8 V (b). (D) Nyquist plot before (a), and after (b) stability test of 1000 cycles.

Table 4.3. Performance comparison of the date leaves derived submicron/nano carbon-based symmetric supercapacitor device with that of previously reported biomass-derived carbon-based supercapacitors.

PANI modified material	Electrolyte	Current density (mA/cm²)	Areal capacitance (mF/cm²)	Energy density (μW/h cm²)	Power density (μW/cm²)	Ref.
CNF/CNT/PANI	H ₃ PO ₄ /PVA	0.5	67.31	-	-	[276]
VACNT/PANI	1 M Na ₂ SO ₄	0.25	16.17	-	-	[277]
PANI/graphene	H ₃ PO ₄ /PVA	0.1	(230 at 0.1 mA/cm ²) (163 at 1mA/cm ²)	14.1 – 37.2 (0.6 to 10 mA/cm ²)	0.9–15 mW/cm ² (0.6 to 10 mA/cm ²)	[278]
PANI/rGO/carbon cloth	1 M H ₂ SO ₄	0.5	470	-	-	[279]
PANI/CNTs/Graphene	1 M H ₂ SO ₄	1.5	790	-	-	[280]
CNT/PANI	H ₂ SO ₄ /PVA	1	184.6	-	-	[281]

hydrogel						
RGO/PANI	H ₃ PO ₄ /PVA	0.1	23	-	-	[282]
Graphite nanosheets/PANI	H ₂ SO ₄ /PVA	0.5	355.6	320	54 mW/cm ²	[283]
Cellulose nanofiber/[PANI-I-RGO]	H ₂ SO ₄ /PVA	0.0043	5.86	-	-	[284]
Cellulose nanofiber/[PANI-I-PEDOT]	H ₂ SO ₄ /PVA	0.0043	4.22	-	-	[284]
PANI/SME (in PW 0 – 0.4 V)	0.1 M H ₂ SO ₄	1	~ 353	~26.4	~400	This work
PANI/SME (in PW 0 – 0.8 V)	0.1 M H ₂ SO ₄	1	~ 297	~7.8	~199	This work

4.4 Conclusion

The morphological and structural characterizations confirm the electrodeposition of PANI throughout a cross-sectional fibril network providing a high active surface area on steel mesh. The optimization study indicates that 15 cycles of the PANI deposition using CV are a suitable cycle number to prepare a stable PANI/SME electrode with a high capacitance performance. The final symmetric supercapacitor was fabricated by applying two symmetrical electrodes of PANI/SME separated by a separator saturated by 0.1 M

H₂SO₄. The PANI/SME electrodes-based symmetric supercapacitor was tested for two ranges of 0 - 0.4 V and 0 - 0.8 V. For the potential window of 0 to 0.4 V; the supercapacitor displayed a maximum areal capacitance (353 mF cm⁻²) for a current density of 1 mA cm⁻² and a maximum energy density (7.8 μW h Kg⁻¹) at a power density (199 μW Kg⁻¹). For the other potential window of 0 to 0.8 V, the supercapacitor displayed a maximum areal capacitance of 297 mF cm⁻² at a current density of 1 mA cm⁻² and a maximum energy density of ~26.4 μW h Kg⁻¹ at a power density of ~400 μW Kg⁻¹. In addition, the PANI/SME based supercapacitor was tested for stability over 1000 GCD cycles, and the supercapacitor does not show any noticeable change. Thus, the fabricated symmetric supercapacitor offers an inexpensive tool for storage energy due to the use of common low-cost steel mesh as a substrate and the active material of electrode of PANI, which is deposited electrochemically. The PANI/SME electrodes-based symmetric supercapacitor is an ideal candidate energy storage tools for mass production.

CHAPTER 5

Date leaves-derived submicron/nano carbon-modified glassy carbon electrode for highly sensitive and simultaneous detection of 1-Naphthol and 2- Naphthol

5.1 Introduction:

As stated previously, the morphological and structure study of the ball-milled date leave carbon shows the particles size of the carbon is in the ranges between 50 to 250 nanometers. In addition, the surface of the carbon particles is scaly rough with small sharp bumps. Consequently, Date leaves derived submicron-nano carbon (DLSNC) is an ideal surface for chemical sensing purposes. In this part of the work, (DLSNC) is used to detect 1-Naphthol (1-NP) and 2-Naphthol (2-NP) simultaneously.

For the detection, a three-electrode system was used. The electrochemical cell contains reference, counter and working electrodes. To fabricate the working electrode, the Glassy carbon electrode GCE modified with DLSNC was selected to detect 1-NP and 2-NP simultaneously.

5.2 Experimental section

5.2.1 Materials

1-NP and 2-NP were obtained from Sigma-Aldrich. Hydrochloric acid (HCl) and H₂SO₄ were obtained from MACRON. Acetic acid, perchloric acid (HClO₄), acetic acid (CH₃COOH), and nitric acid (HNO₃) were procured from Sigma-Aldrich. Phosphoric acid (H₃PO₄) was obtained from Fluka. All the equipment and glasses were cleaned and rinsed with distilled water, and the chemical solutions were prepared using deionized (DI) water.

5.2.2 DLSNC/GCE electrode

A DLSNC solution (1 mg/ml) was prepared using DI water with ultrasonication for 30 minutes. 10 µL of the prepared DLSNC solution was dispensed on the clean GCE and was dried at room temperature over 12 hours. The resultant modified electrode is denoted as DLSNC/GCE in the rest of this thesis paper.

5.2.3 Electrochemical measurements

Different electrochemical measurements were done using the three electrodes system (Figure 5.1). The measurements of the experiments were performed with an electrochemical workstation (CHI440). An Ag/AgCl reference electrode, a platinum wire counter electrode, and GCE or DLSNC/GCE fabricated electrode as working electrodes were used. The measurements were performed in phosphate buffer solutions in different pH and different acids without degassing (in the presence of oxygen).

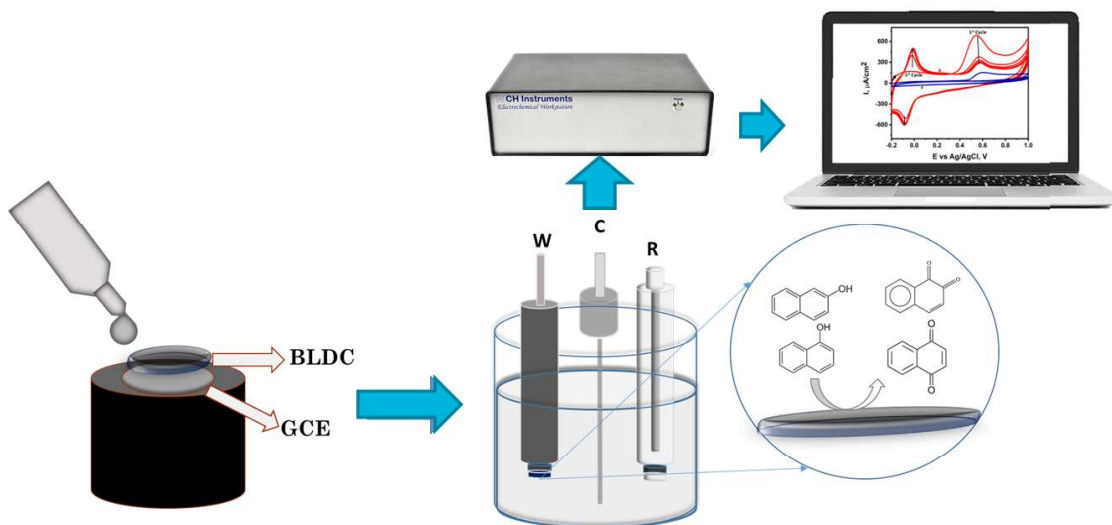


Figure 5.1. BLDC/GCE based electrochemical sensor fabrication to detect 1-NP and 2-NP simultaneously.

5.3 Results and discussion

5.3.1 Electrochemical study

The electrocatalytic performances of DLSNC/GCE is evaluated by recording the CVs in phosphate buffer pH 7 in the presence of 0.5 mM of 1-NP and 0.5 mM 2-NP in the potential window (PW) from 0.1 to 1.0 V (Figure 5.2). The voltammogram showed two anodic peaks at 0.38 V and 0.56 V due to the oxidation of 1-NP into 1,4-naphthoquinone and oxidation of 2-NP into 1,2-naphthoquinone, respectively. Two separated oxidation peaks could be used as characteristic peaks for qualitative analysis of 1-NP and 2-NP simultaneously. Furthermore, the current produced of the oxidation peaks could be used for quantitative analysis of 1-NP and 2-NP concentrations.

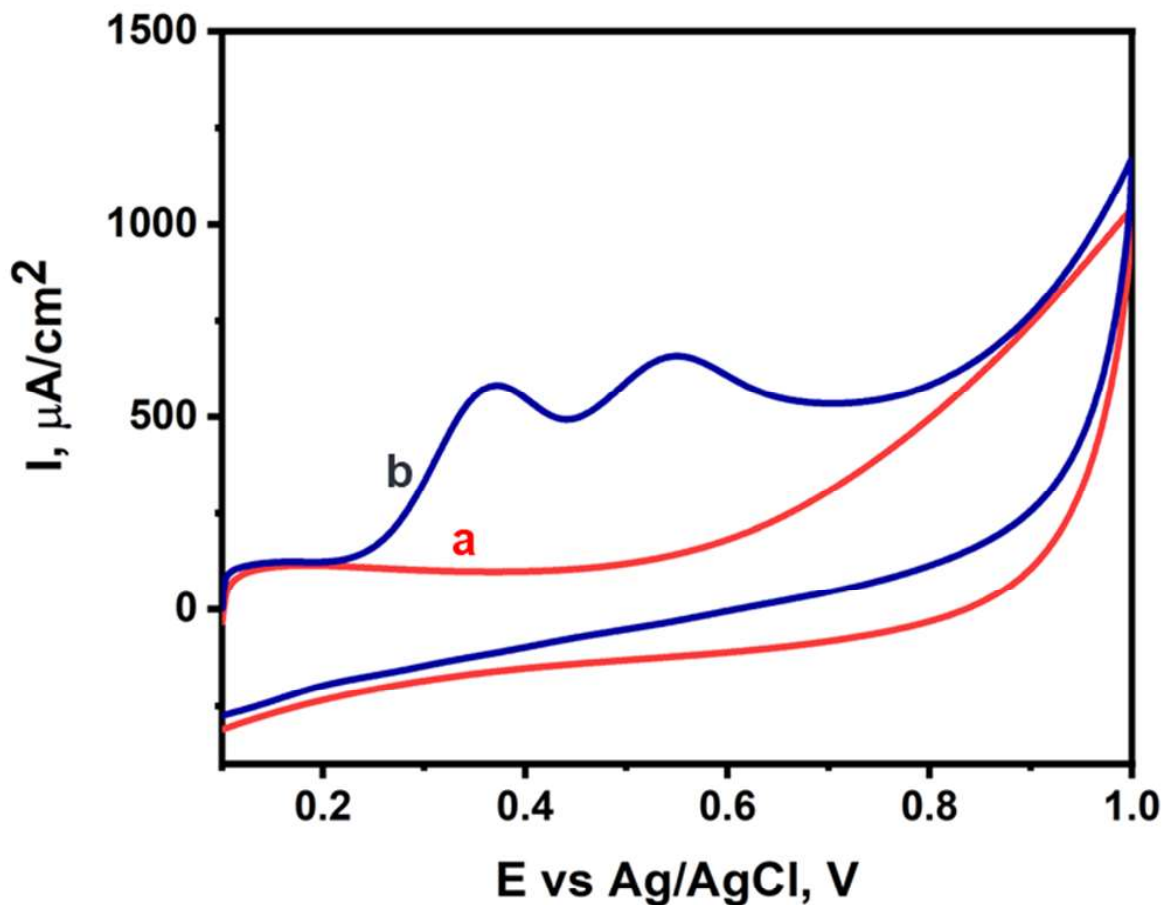


Figure 5.2. CVs of DLSNC/GCE in phosphate buffer pH 7 in the absence (a) and presence (b) of 0.5 mM of 1-NP and 0.5 mM 2-NP.

For a deeper investigation of the electrochemical performances of DLSNC/GCE, the two electrodes of DLSNC/GCE and GCE were tested by recording the CVs of five cycles in phosphate buffer pH 7 in the presence of 0.5 mM 2-NP in the PW from -0.2 to 1.0 V (Figure 5.3). The DLSNC/GCE voltammogram showed an anodic peak of 0.58 V associated with the oxidation of 2-NP to 1,2-naphthoquinone, as mentioned previously. It was observed that the oxidation peak at 0.56 V decreased sharply in the second cycle and continued decreasing for the rest of the cycles. Furthermore, the voltammogram showed a redox peak at -0.08 and -0.03 V corresponding to reduction and oxidation peaks,

respectively. The reduction peak corresponds to the reduction of the generated 1,2-naphthoquinone to 1,2-dihydroxy naphthalene. While the oxidation peak corresponds to the reverse reaction of the oxidation of 1,2-dihydroxy naphthalene to 1,2-naphthoquinone. The redox peaks increased throughout the measurement due to the continuous absorption of 1,2-naphthoquinone and 1,2-dihydroxy naphthalene. This in turn decreases the amount of 2-NP oxidized on the electrode surface due to being occupied by the adsorbed 1,2-naphthoquinone leading to the continuous decrease in 2-NP oxidation peak current. In the case of GCE, the voltammogram showed an anodic peak (0.56 V) related to the oxidation of 2-NP to 1,2-naphthoquinone with a significant low current compared to the DLSNC/GCE. In addition, no additional redox peaks were observed on the surface of GCE. This indicates the special electrochemical properties of DLSNC/GCE toward the reduction of the 1,2-naphthoquinone and oxidation 1,2-dihydroxy naphthalene.

Similarly, in the presence of the 1-NP, the 1-NP shows the same behavior with regards to the direct oxidation peak and redox peaks. In the first cycle the 1-NP is oxidized to 1,4-naphthoquinone on DLSNC/GCE surface at 0.38 V (Figure 5.4). The redox peaks corresponding to 1-NP were at -0.2 and -1.5 V corresponding to reduction and oxidation peaks, respectively. The reduction peak corresponding to the reduction of 1,4-naphthoquinone to 1,4-dihydroxy naphthalene. While the oxidation peak corresponds to the reverse reaction of the oxidation of 1,4-dihydroxy naphthalene to 1,4-naphthoquinone. The redox peaks increased throughout the measurement showing the same behavior in the case of presence of 1-NP.

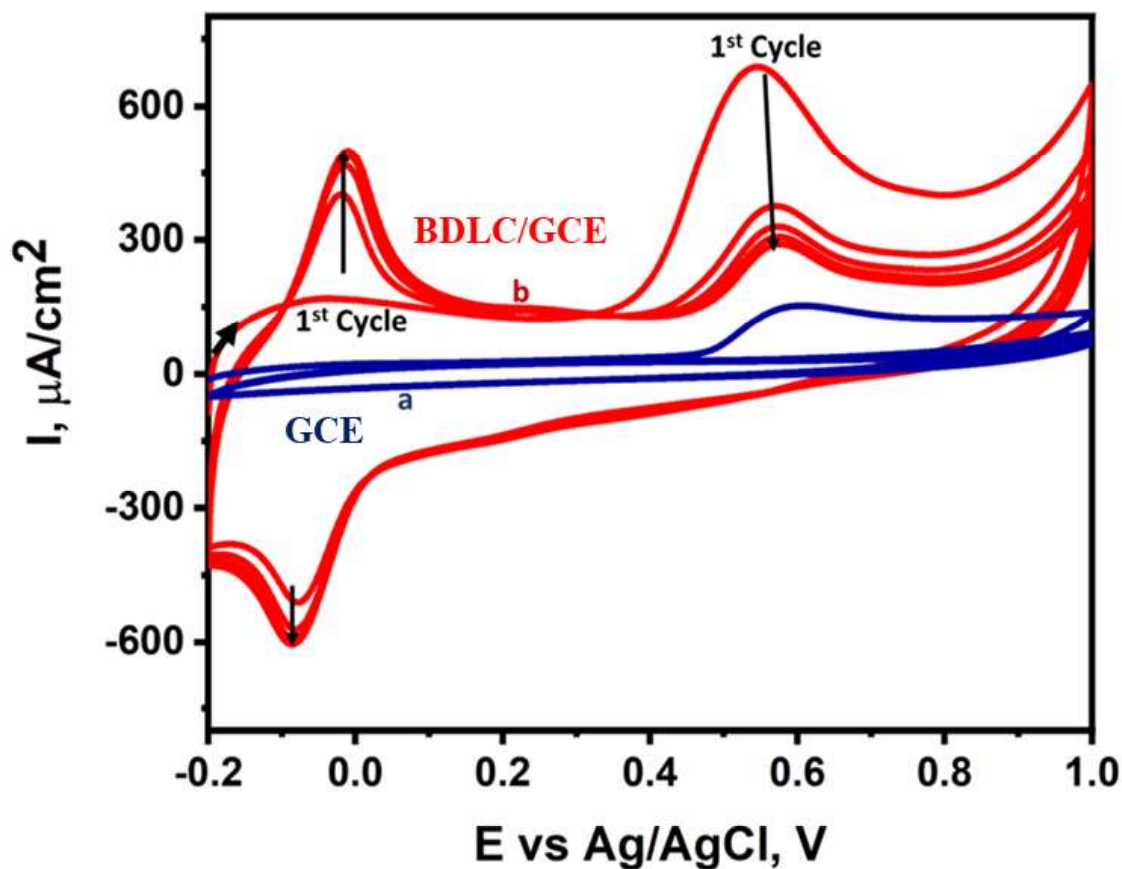


Figure 5.3. CVs of 5 cycles of GCD (a) and DLSNC/GCE (b) in presence of 0.5 mM 2-NP in 100 μ M phosphate buffer pH of 7.

(Figure 5.4) shows CVs of ten cycles of GCE-DLSNC in 100 mM phosphate buffer pH 7, 0.5 mM 1-NP and 0.5 mM 2-NP. According to voltammogram, there are two oxidation peaks at 0.38 and 0.56 V corresponding to 1-NP and 2-NP oxidations, respectively. Furthermore, the voltammogram shows two groups of redox peaks. The first redox peaks related to the presence of 2-NP were at -0.1 and -0.03 V corresponding to reduction and oxidation of 1,2-naphthoquinone to 1,2-dihydroxy naphthalene. While the second redox peaks related to the presence of 1-NP were at -1.5 and -0.2 V corresponding to reduction and oxidation of 1,4-naphthoquinone to 1,4-dihydroxy naphthalene.

According to the results, two detection methods of 1-NP and 2-NP simultaneously could be designed based on the fabricated DLSNC/GCE sensor. The first method (direct electrooxidation) is based on measuring the directed oxidation reaction of 1-NP and 2-NP at 0.38 and 0.56 V. The method measures the oxidation peaks current using CV for 1 cycle from 0.1 to 1.0 V. The second method (quinone formation) is based on measuring the oxidation peaks of 1,4-dihydroxy naphthalene into 1,4-naphthoquinone and 1,2-dihydroxy naphthalene into 1,2-naphthoquinone to evaluate the concentrations of 1-NP and 2-NP, respectively.

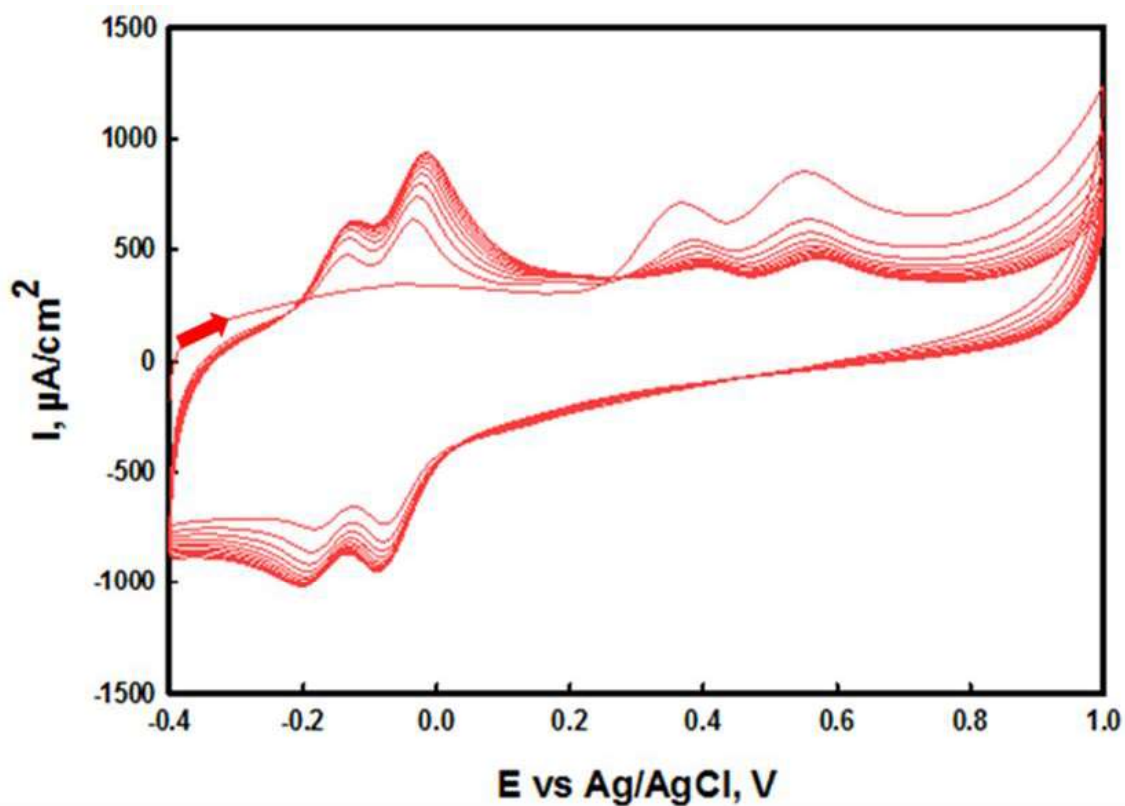


Figure 5.4. CVs of 10 cycles of GCE- DLSNC in 100 mM phosphate buffer pH 7, 0.5 mM 1-NP and 0.5 mM 2-NP.

To improve the analytical performance of the BELC/GCE sensor using the direct oxidation method, different phosphate buffer solution with different pH values of 6, 7, 8, 9, 10 were tested to optimize the oxidation signal (Figure 5.5). The phosphate buffer solution pH 8 was selected as an optimized electrolyte for the method due to the high oxidation 1-NP and 2-NP oxidation current compared with the current at different pHs. Furthermore, Figure 5.5 shows expected positive shift of oxidation peak potential of 1-NP and 2-NP by increasing pH. The pH value versus oxidation peak potential was plotted for 1-NP and 2-NP oxidation separately. The linear equation of pH vs oxidation peak potential was ($E = -0.0637 \text{ pH} + 0.8244$) for the oxidation of 1-NP and ($E = -0.0665 \text{ pH} + 1.0308$) for the oxidation of 2-NP. The slopes value of the linear equations is -0.0637 and -0.0665 for oxidation of 1-NP and 2-NP, respectively. Due to the slope values are close to the Nernstian value which is 0.059 V pH^{-1} . This in turn indicates an equivalent number of electrons and protons transfer through the oxidation reactions of 1-NP and 2-NP.

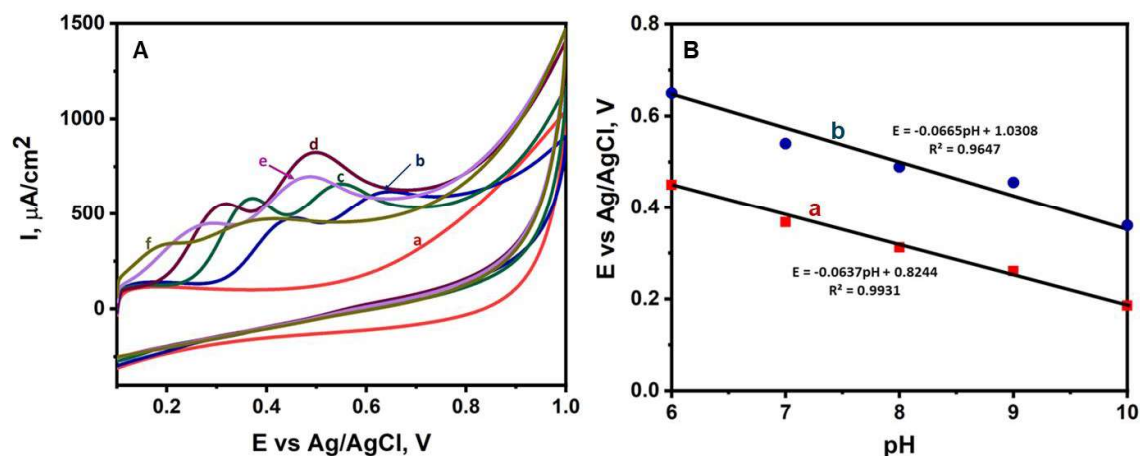


Figure 5.5. CVs of DLSNC/GCE in the absence (a), or presence of 0.5 mM 1-NP and 0.5 mM 2-NP in 0.1 M phosphate buffer at pH 7.

The analytical performance of DLSNC/GCE using the direct oxidation method was evaluated for 1-NP detection in the presence of fixed concentration of 2-NP of 100 μM (Figure 5.6). The calibration curve was plotted indicates a dynamic range from 25 to 300 μM . The linear equation is:

$$I = 1.0579 [1\text{-NP}] + 95.146 \text{ with } R^2 = 0.9843.$$

The Limit of quantification (LOQ) is 25 μM and the limit of detection (LOD) is 14 μM , and the reducibility is 4.7%.

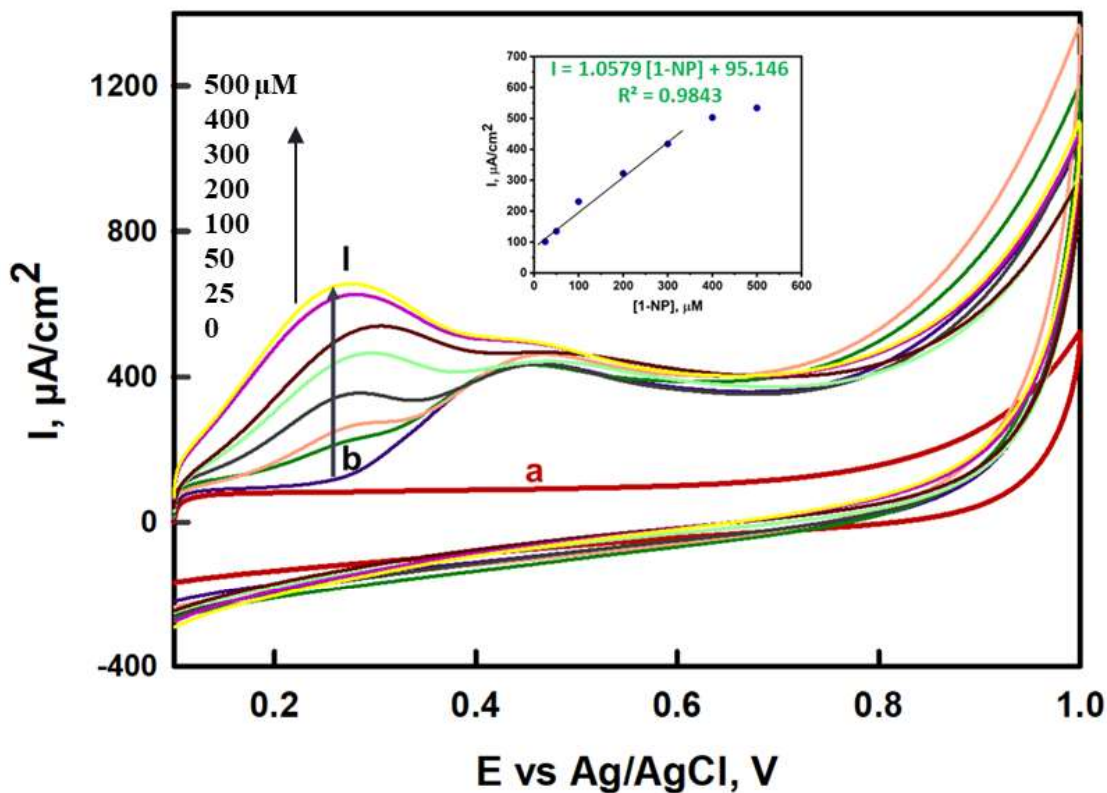


Figure 5.6. CVs of DLSNC/GCE in 100 mM phosphate buffer pH 8 in the absence (a), or presence of 100 μM 2-NP and 0 (b), 25 (c), 50 (d), 100 (e), 200 (f), 300 (g), 400 (k), 500 μM (l) of 1-NP.

The analytical performance of the DLSNC/GCE using the direct oxidation method was evaluated for 2-NP detection in the presence of fixed concentration of 1-NP of 100 μM (Figure 5.7). The calibration curve was plotted indicates a dynamic range from 25 to 200 μM . the linear equation is:

$$I = 1.1022 [2\text{-NP}] + 17.97 \text{ with } R^2 = 0.9984.$$

The Limit of quantification (LOQ) is 25 μM and the limit of detection (LOD) is 11 μM , and the reducibility is 4.4%.

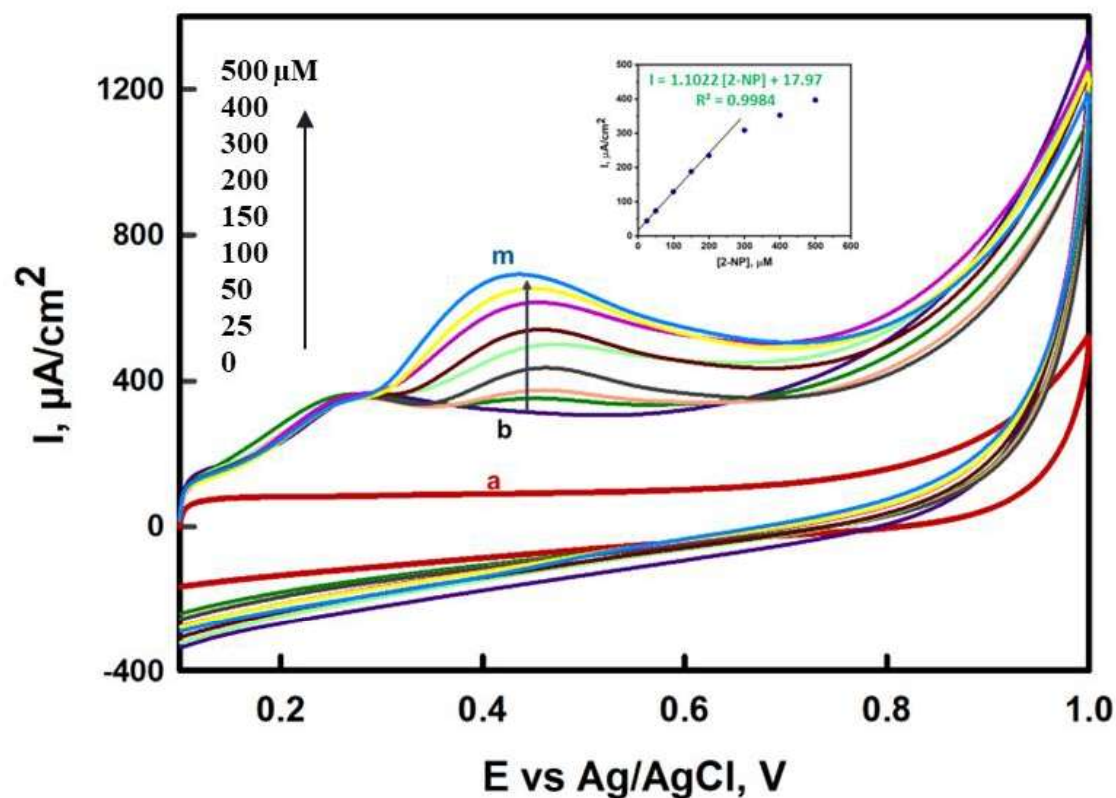


Figure 5.7. CVs of DLSNC/GCE in 100 mM PB at pH 8 in the absence (a), or presence of 100 μM 1-NP and 0 (b), 25 (c), 50 (d), 100 (e), 150 (f), 200 (g), 300 (k), 400 (l), 500 μM (m) of 2-NP.

The analytical performance of the DLSNC/GCE using the second method of (via quinone formation) was based on the evaluate the oxidation peaks current in the redox peaks after optimized 50 cycles for 1-NP and 2-NP simultaneously (Figure 5.8). To improve the analytical performance, the DLSNC/GCE was checked in the acidic medium of 1 M HClO_4 and compared with the analytical performance in phosphate buffer pH 8. According to the voltammograms, the sensor shows a significant enhancement related to the redox peaks in acidic medium compared with the sensor performance in the phosphate buffer pH 8.

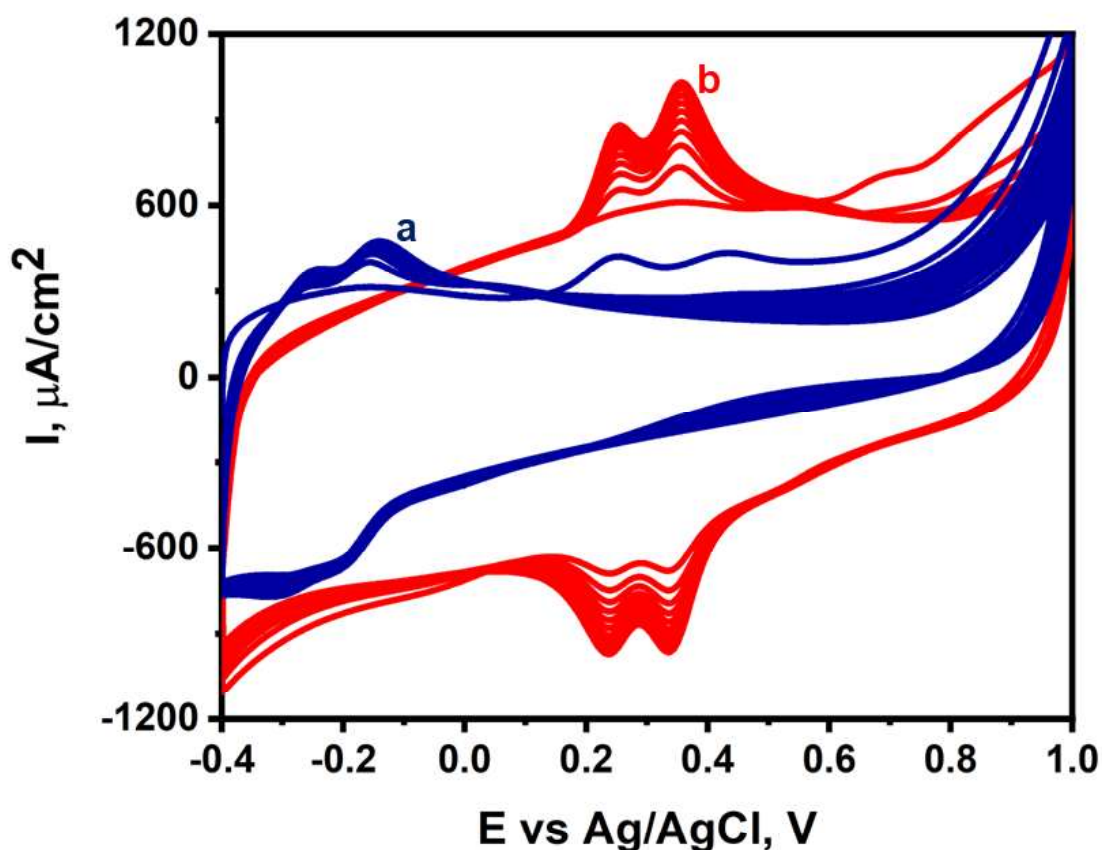


Figure 5.8. CVs of 10 cycles of DLSNC/GCE in 0.1 M PB buffer at pH 8 (a), and in 1 M HClO_4 (b) in the presence of 50 μM 1-NP and 50 μM 2-NP.

Six various acids were checked as an electrolyte for the DLSNC/GCE using the second method of (via quinone formation) in the presence of 50 μM of 1-NP and 50 μM 2-NP (Figure 5.9). The tested set of acids includes HCl, HNO₃, HClO₄, CH₃COOH, H₃PO₄, and H₂SO₄. The highest oxidation signals were measured by using 1 M of HClO₄. Furthermore, different concentrations of HClO₄ including 0.1, 0.5, and 1.0 M (Figure 5.10). The measurement shows the oxidation signals in the presence of 50 μM of 1-NP and 50 μM 2-NP were increased by increasing the concentration of the HClO₄. The concentration of 1 M was selected as an optimum. The higher concentration of 1 M leads to high noise in the voltammograms which indicates instability of the electrode in a higher concentration of the acid.

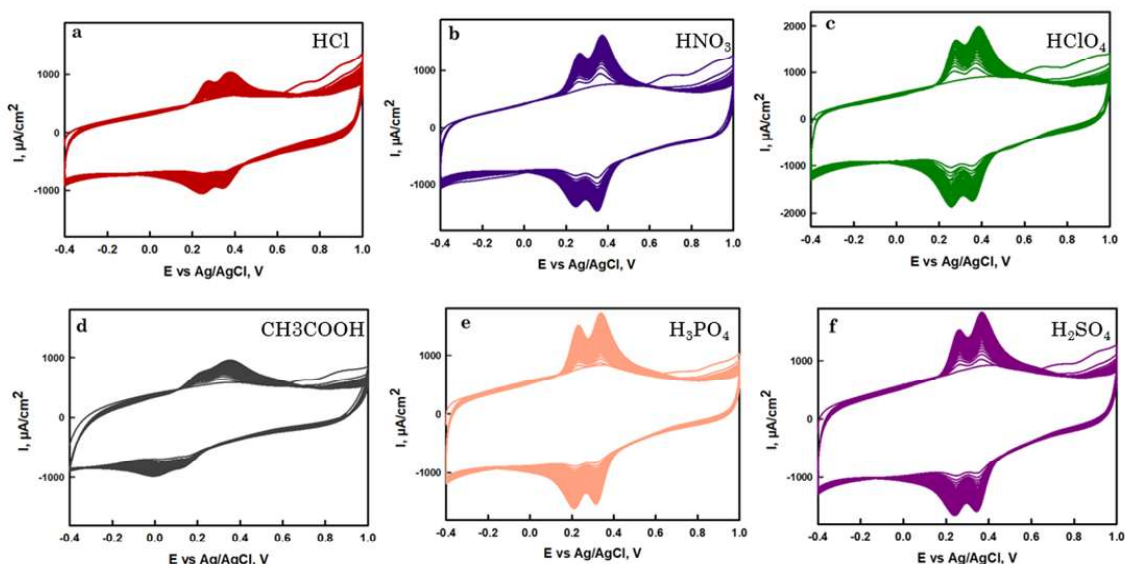


Figure 5.9. CVs of 50 cycles of DLSNC/GCE in presence of 50 μM of 1-NP and 50 μM 2-NP in 1M HCl (a), HNO₃ (b), HClO₄ (c), CH₃COOH (d), H₃PO₄ (e), and H₂SO₄ (f).

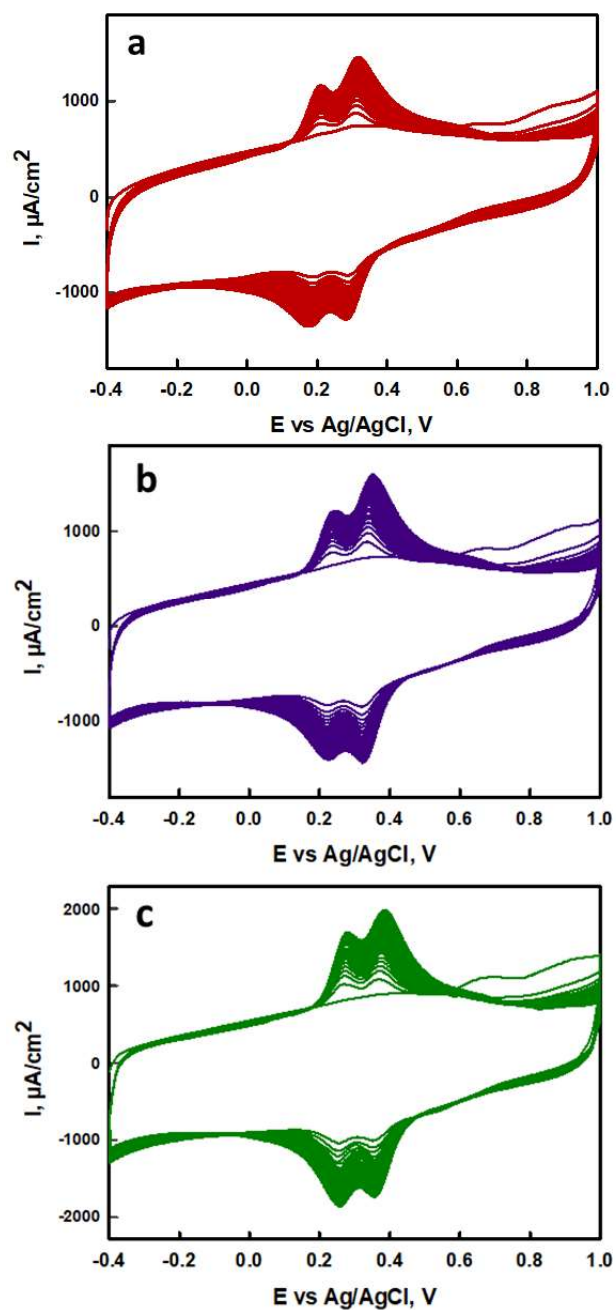


Figure 5.10. CVs of 50 cycles of DLSNC/GCE in presence of 50 μM of 1-NP and 50 μM 2-NP in HClO_4 of Concentration of 0.1 (a), 0.5 (b), and 1 M (c).

The analytical performance of the DLSNC/GCE using the second method of (via quinone formation) was evaluated for 1-NP detection in the presence of fixed concentration of 2-NP of 10 μM (Figure 5.11). The calibration curve was plotted indicates a dynamic range from 1 to 25 μM . The linear equation is:

$$I = 25.626 [1\text{-NP}] + 237.62 \text{ with } R^2 = 0.9842.$$

The Limit of quantification (LOQ) is 1 μM and the limit of detection (LOD) is 0.64 μM , and the reducibility is 7.5%.

Similarly, the analytical performance of the DLSNC/GCE using the second method of (via quinone formation) was evaluated for 2-NP detection in the presence of fixed concentration of 1-NP of 10 μM (Figure 5.12). The calibration curve was plotted indicates a dynamic range from 1 to 25 μM . the linear equation is:

$$I = 26.445 [2\text{-NP}] + 52.949 \text{ with } R^2 = 0.981.$$

The Limit of quantification (LOQ) is 1 μM and the limit of detection (LOD) is 0.61 μM , and the reducibility is 7.1%.

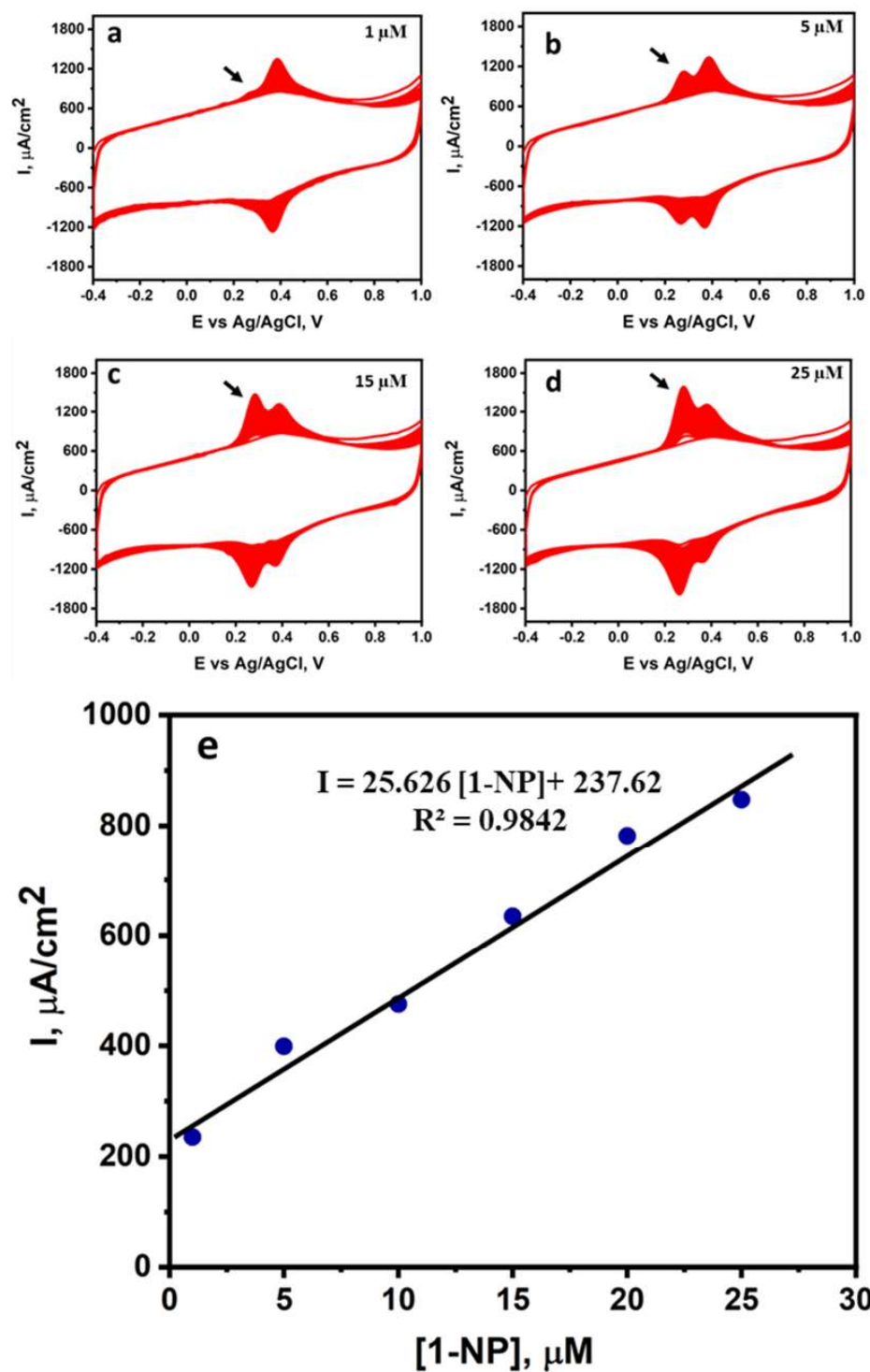


Figure 5.11. CVs of 50 cycles of DLSNC/GCE in 1 M HClO₄ in the absence (a), or presence of 10 μM 2-NP and 1 (a), 5 (b), 15 (c), and 25 μM (d) of 1-NP.

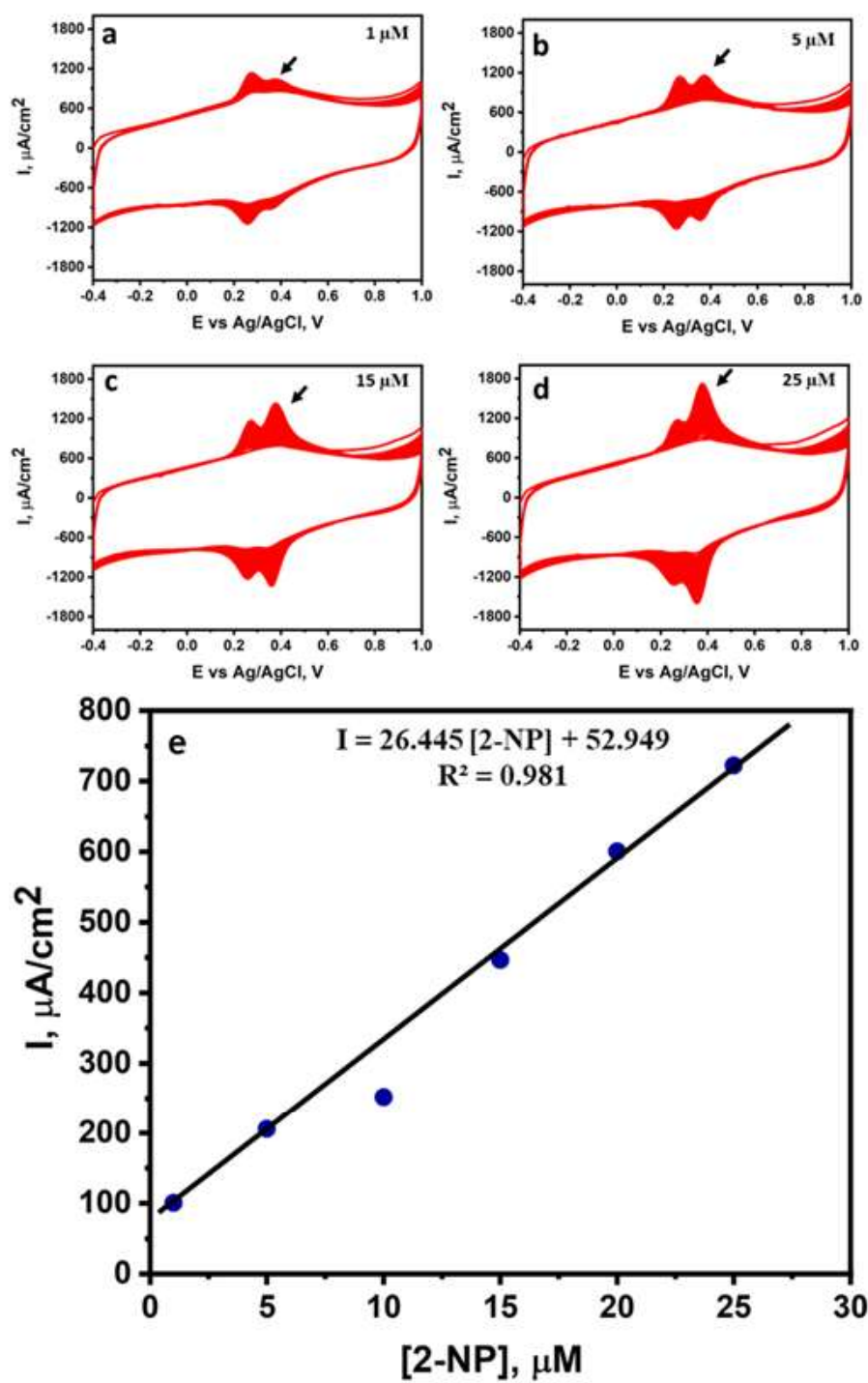


Figure 5.12. CVs of 50 cycles of DLSNC/GCE in 1 M HClO_4 in the absence (a), or presence of 10 μM 1-NP and 1 (a), 5 (b), 15 (c), and 25 μM (d) of 2-NP.

5.4 Conclusion

In summary, electrochemical sensor for simultaneous detection 1-NP and 2-NP was fabricated using DLSNC/GCE as a working electrode, Ag/AgCl as a reference electrode, and a Pt wire as a counter electrode. The study provides two methods which can be used as electrochemical sensor. The first method is based on the direct oxidation of 1-NP and 2-NP. The second method is based on redox peaks due to the quinone formation. The analytical performance of the fabricated electrochemical sensor shows a high analytical performance toward 1-NP and 2-NP including:

LOD of 1-NP: 14 μM (direct electrooxidation) and 0.64 μM (quinone formation).

LOQ of 1-NP: 25 μM (direct electrooxidation) and 1 μM (quinone formation).

LOD of 2-NP: 11 μM (direct electrooxidation) and 0.61 μM (quinone formation).

LOQ of 2-NP: 25 μM (direct electrooxidation) and 1 μM (quinone formation).

CHAPTER 6

CONCLUSION AND FUTURE RECOMMENDATIONS

6.1 Conclusion

Submicron-nanocarbon from date leaves has been prepared via pyrolysis and ball milling. The developed method for preparing submicron-nanocarbon is scalable. According to the morphological characterization using FESEM, the synthesized carbon particles are in the range of 50 to 200 nm. In addition, The EDS indicates the exitance of C, Si, K, Na, S, O due to the plant resource of the carbon, and Zr as a trace from the grinding balls throughout the ball-milling process. The XRD displays the amorphous structure of the carbon in addition to some amount of crystalline graphitic carbon. The FTIR indicates the exitance of SP³ and SP² carbon and an oxygen content as functional groups of carbonyl and ether.

The synthesized carbon was used successfully to prepare a supercapacitor. Electrochemical investigations of the DLSNC/Steel electrode by CV measurements in a three-electrode system indicate that acid of H₂SO₄ with a concentration of 0.1 M is a suitable electrolyte for the supercapacitor. The final symmetric supercapacitor was fabricated successfully by applying two symmetrical electrodes of DLSNC/Steel separated by a separator saturated by H₂SO₄ (0.1M). The symmetric DLSNC/Steel device

exhibited a specific capacitance (107 F/g). The supercapacitor energy density and a power density were 10 Wh/Kg and 200 W/Kg, respectively.

In the second part, The PANI/SME electrodes-based symmetric supercapacitor was fabricated by electrochemical deposition of PANI on the steel mesh strips using CV for optimized 15 cycles method. To fabricate the PANI/SME device a separator saturated with 0.1 M H₂SO₄ was sandwiched between two PANI/SME electrodes. The PANI/SME electrodes-based symmetric supercapacitor was tested for two ranges of 0 - 0.4 V and 0 - 0.8 V. For the measured range of 0 - 0.4 V; the supercapacitor displayed a maximum areal capacitance of $\sim 353 \text{ mF cm}^{-2}$ at a current density of 1 mA cm^{-2} and a maximum energy density of $\sim 7.8 \text{ } \mu\text{W h Kg}^{-1}$ at a power density of $\sim 199 \text{ } \mu\text{W Kg}^{-1}$. For the other potential window of 0 to 0.8 V, the supercapacitor showed a maximum areal capacitance of 297 mF cm^{-2} for a current density of 1 mA cm^{-2} and a maximum energy density of $26.4 \text{ } \mu\text{W h Kg}^{-1}$ at a power density of $\sim 400 \text{ } \mu\text{W Kg}^{-1}$. In addition, the PANI/SME based supercapacitor was tested for stability over 1000 GCD cycles, and the supercapacitor does not show any noticeable change.

Furthermore, the synthesized carbon from date palm leaves was used successfully to fabricate a chemical sensor to detect 1-NP and 2-NP. The electrochemical sensor was fabricated using DLSNC/GCE as a working electrode, Ag/AgCl as a reference electrode, and a Pt wire as a counter electrode. Two methods were developed based on the fabricated electrochemical sensor. The first method is based on the direct oxidation of 1-NP and 2-NP. The second method is based on redox peaks due to the quinone formation.

The analytical performance of the DLSNC/GCE using the direct oxidation method was evaluated for 1-NP detection in the presence of fixed concentration of 2-NP of 100 μM . The Limit of quantification (LOQ) is 25 μM and the limit of detection (LOD) is 14 μM , and the reproducibility is 4.7%. while the analytical performance of the DLSNC/GCE for 2-NP detection in the presence of fixed concentration of 1-NP of 100 μM . LOQ is 25 μM and LOD is 11 μM , and the reproducibility is 4.1%.

The analytical performance of the DLSNC/GCE using the second method of (via quinone formation) was evaluated for 1-NP detection in the presence of fixed concentration of 2-NP of 10 μM . LOQ is 1 μM and LOD is 0.64 μM , and the reducibility is 7.5%. Furthermore, the analytical performance of the DLSNC/GCE using the second method of (via quinone formation) was evaluated for 2-NP detection in the presence of fixed concentration of 1-NP of 10 μM . LOQ is 1 μM and LOD is 0.61 μM , and the reducibility is 7.1%.

6.2 Future Recommendations

The main outcome of the work was utilization of the prepared date leaves-derived carbon for supercapacitor and phenolic compounds chemical sensor applications. This in turn proposes the follow future recommendations:

1. Utilization of the prepared date leaves-derived carbon in other areas such as sensor fabrication for other analytes.
2. Utilization of the prepared date leaves-derived carbon Anticorrosion coating development

3. Checking the ability of the date leaves-derived carbon to use as printing ink and finding the suitable method for preparation.
4. Utilization of the prepared date leaves-derived carbon in Battery fabrication
5. Due to the morphological and structure characterization which confirms the existence of heteroatoms and some functional groups the date leaves-derived carbon could be used successfully for catalytic applications.
6. Development of composite with the prepared date leaves-derived carbon for enhancing the properties of the materials for many applications.
7. Fabrication of prototype Naphthol sensor.
8. Fabrication of prototype supercapacitor.

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- 01. Preparation and Electrochemical Properties of a Gallium-Doped Zinc Oxide Electrode Decorated with Densely Gathered Palladium Nanoparticles
DOI: 10.1149/2.0461602jes
- 02. Electrochemical Investigation of Metal Oxide Conducting Electrodes for Direct Detection of Sulfide
DOI: 10.1002/elan.201400539
- 03. From Electrode Surface Fouling to Sensitive Electroanalytical Determination of Phenols
DOI: 10.1002/elan.201300101

- 04. Preparation of Indium Tin Oxide Nanoparticle-modified 3-Aminopropyltrimethoxysilane-functionalized Indium Tin Oxide Electrode for Electrochemical Sulfide Detection
DOI: 10.1002/elan.201700058
- 05. Enhanced oxygen evolution via electrochemical water oxidation using conducting polymer and nanoparticle composites
DOI: 10.1002/asia.202001163
- 06. Mechanistic insights of the oxidation of bisphenol A at ultrasonication assisted polyaniline-Au nanoparticles composite for highly sensitive electrochemical sensor
DOI: 10.1016/j.electacta.2021.137968
- 07. Electrodeposition of polyaniline on high electroactive indium tin oxide nanoparticles-modified fluorine doped tin oxide electrode for fabrication of high-performance hybrid supercapacitor.
DOI: 10.1016/j.arabjc.2022.104058
- 08. Gold Nanomaterials and their Composites as Electrochemical Sensing Platforms for Nitrite Detection.
DOI: 10.1002/asia.202200823
- 09. Water-based Inkjet Inks Formulation using Jute Stick-derived Submicron Carbon Particles
DOI: 10.1002/asia.202200869

- 10. Fabrication of high-performance supercapacitor using date leaves-derived submicron/nanocarbon.

DOI: 10.1016/j.jscs.2022.101570.

- 11. Designing High-performing Symmetric Supercapacitor by Engineering Polyaniline on Steel Mesh Surface via Electrodeposition.

DOI: 10.1002/asia.202201223.

- 12. A High-Energy Asymmetric Supercapacitor Based on Tomato-Leaf-Derived Hierarchical Porous Activated Carbon and Electrochemically Deposited Polyaniline Electrodes for Battery-Free Heart-Pulse-Rate Monitoring.

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Patents:

- 1. “Method for preparing a gallium-doped zinc oxide electrode decorated with densely gathered palladium nanoparticles” US Patent number: US 10,161,052 B2.
- 2. “Aqueous solution method for manufacturing palladium doped electrode” US Patent number: US 10,844,499 B2.
- 3. “Method for making a Pd-doped zinc oxide conducting electrode” US Patent number: US 10,844,500 B2.

Book Chapters:

- 01. Co-authoring a full chapter under the title (Conducting polymers-based nanocomposites for supercapacitors) pp485-511 in the book titled (Nanostructured Materials for Supercapacitors)

https://link.springer.com/chapter/10.1007/978-3-030-99302-3_22

- 02. First authoring a full chapter under the title (Biomass-carbon PCs based supercapacitors) in the book titled (Biomass-carbon based supercapacitors). In preparation.
- 03. Co-authoring a full chapter under the title (types of supercapacitors) in the book titled (Biomass-carbon based supercapacitors). In preparation.

Conferences:

- 01. Shared in 245TH American chemical society (ACS) NATIONAL MEETING, USA, NEW ORLEANS, April 7–11. 2013 with the poster under the title: Design and Fabrication of Lateral-Flow Chromatographic Strips for Analytical/Sensing Application
- 02. Submitted a paper to the Fifth Saudi Science Conference (SSC5) -2014 under the title: Magnetic Bead-Based Electrochemical Immunoassay to Detect Rabbit IgG Antigen
- 03. S.A. Dina, M.M. Hasan, T. Islam, A. Imran, B. Alqahtani, S.S. Shah, W. Mahfoz, M.R. Karime, H.F. Alharbi, Md. Abdul Aziz and A. J. Saleh Ahammad*, Ultrasonication assisted polyaniline-Au nanoparticles composite as a sensing material for electrochemical detection of bisphenol A, 2021 American Chemical Society Eastern U.S. Younger Chemists Committee Virtual Research Symposium, 2-6August, 2021, (Oral presentation, ANYL A2-4.
- 04. Represented a paper to (E-SENSOL) 2022 International E-Symposium on Sustainable Energy: Advances and developments (virtual modality) in The Autonomous University of Nuevo León, Mexico. During July 06 to 08, 2022, through

the Microsoft TEAMS platform with a verbal presentation under the title: Electrodeposition of polyaniline on steel mesh for fabrication of high-performance symmetric supercapacitor.